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AN EXPERIMENTAL INVESTIGATION OF CHEMICAL REACTIONS INVOLVING MUONIUM

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The asymmetry coefficients in the angular distribution of positrons emitted in μ–e decays are measured for a number of compounds and their binary mixtures. The rate constants for the interaction between atomic muonium and matter are computed on the basis of the results obtained. The method of competing acceptors for parallel reactions is employed with the aim of raising the accuracy of the measurements and elucidating the mechanism of the processes. The dependences of the asymmetry coefficients on the magnetic field strength are measured for a number of compounds. The data are discussed within the framework of the picture of chemical reactions with muonium.

1. INTRODUCTION

In earlier papers[1, 2] we developed on the basis of the published data a picture of chemical interactions between muonium and matter. The chemical reactions between atomic muonium and molecules of a medium in which polarized μ^+ mesons are decelerated and stopped leads to a decrease in the depolarization of the μ^+ mesons; this decrease is quantitatively connected with the rate constants of the occurring processes. The rates of the chemical reactions of muonium are thus determined from the experimental asymmetry coefficients in the angular distributions of the positrons of the μ–e decay. Since the muonium atom is similar in its chemical properties to atomic hydrogen, the corresponding calculation (based in the simplest case on collision theory) makes it possible to obtain the absolute values of the rate constants for atomic hydrogen. Among the essential features of this physical method is the possibility of investigating exceedingly rapid chemical reactions, the study of elementary interaction processes, the elimination of the complicating factor of interaction between the free atom and the secondary products of the reaction as a result of the negligibly small depth of transformation of the matter, and the possibility of explaining the mechanism of the occurring processes. A characteristic feature is that the experimental conditions are independent of the aggregate state and of the temperature of the substance, thus greatly adding to the possible number of objects of investigation. This paper reports an experimental verification of the phenomenological picture developed in [1, 2]. To eliminate the possible influence of local magnetic fields in the substance, we used mostly organic compounds in the liquid state.

2. APPARATUS

The setup for the measurement of the asymmetry coefficients (c′) of μ–e decay in various substances is shown in Fig. 1. The transverse magnetic field in which the spin precession of the meson took place was produced by a water-cooled

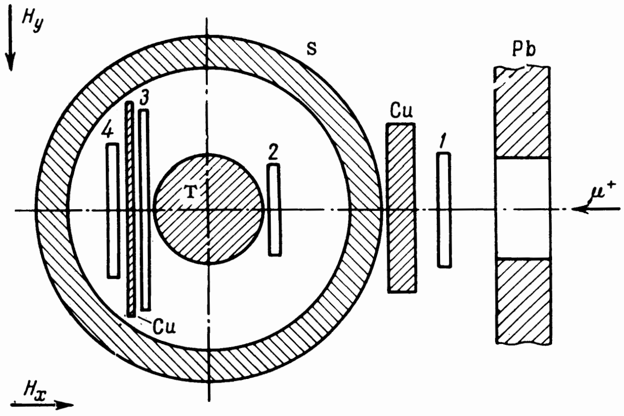

FIG. 1. Diagram of setup. S – solenoid, T – target, 1, 2, 3, 4 – counters.

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solenoid of 30 cm diameter and 60 cm height. The maximum magnetic field intensity reached 300 Oe at an inhomogeneity lower than 0.5% within the limits of the target dimensions.

In measurements in fields lower than 150 Oe, the external magnetic fields were compensated for ($H_z \approx 5$ Oe, H_x, $H_y \leq 1$ Oe). To this end, three pairs of coils were used (not shown in Fig. 1), located along the sides of a cube measuring 1.05 × 1.05 × 1.05 m, in the center of which the target was placed. The solenoid-field calibration and the compensation of the external magnetic fields were effected with permalloy pickups in three perpendicular planes, with accuracy $\pm(0.5\% + 0.05$ Oe). The currents in the solenoid and in the compensating coils was stable to better than 0.5%.

The arrangement and the dimensions of the scintillation counters are shown in Fig. 1. To eliminate the influence of the magnetic field of the solenoid on the photomultipliers (FÉU-36 throughout), 40-cm light pipes of organic glass were used in counters 2, 3, and 4, and also shields made of 10 mm Armco iron.

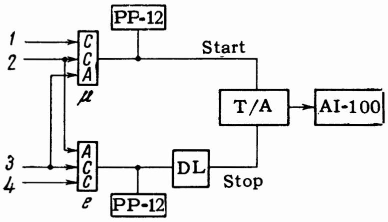

FIG. 2. Block diagram.

The pulses from the photomultipliers were fed to two coincidence circuits (Fig. 2) with resolution time ~20 nsec. The output of one circuit was a pulse produced in accordance with the 1 + 2 – 3 scheme, henceforth called the "μ signal;" the output of the other coincidence circuit was produced the "e-signal" (3 + 4 – 2). These pulses triggered a T/A converter, which transformed the time interval between them into a variable-amplitude signal. The amplitude of the output signal was measured with an AI-100 100-channel pulse-height analyzer. In the case of arrival of a μ-signal only, or of an e-signal beyond the limits of the chosen time range, the amplitude of the output signal was zero. The amplitude increased linearly with decreasing time between the μ and e signals, and corresponded at zero time to the 100th channel of the AI-100. Channel widths of 73.8, 18.9, and 4.9_4 nsec were used in different experiments. The nonlinearity of the scale was smaller than 1%.

The introduction of a delay line (DL) in the e-signal channel, with delays ~1.6, 0.4, and 0.1 μsec (each for the respective range), shifted the time origin from the 100th to the 80th channel. This made it possible to fix simultaneously the background of the random coincidences between the μ and e pulses (channels 80–100) and the distribution of the decay times (channels 80–1).

The probability of registering the decay near the start of the time origin decreased rapidly because of the finite duration (~40 nsec) of the anticoincidence signals of counters 2 and 3. In some cases, especially when working in the 18.9 and 4.9_4 nsec/channel ranges, the e-signal was produced in accordance with the 3 + 4 scheme. This led to a certain increase of the random-coincidence background (by 20–40%), but made it possible to obtain the distribution of the decay time without distortion, starting with 10–20 nsec.

The resolution time of the entire electronic circuit as a whole, measured with the AI-100 instrument with the anticoincidence signals disconnected for all the particles passing through the counters, was not worse than ±5 nsec. The scale linearity and the channel width were calibrated in each series of experiments with random-coincidence pulses in counters 2 (μ-signal) and 3 (e-signal) from a Co^{60} γ-quantum source. The intensity was modulated with a quartz generator at 1.0009 and 4.0036 Mc.[3]

3. TARGETS

The targets were cylindrical duraluminum vessels approximately one liter in volume, 100 mm in diameter, and of wall thickness 0.7 mm. Because of the technological conditions, the targets had identical dimensions and accordingly somewhat different thicknesses in g/cm^2. This changed the energy spectrum of the emitted decay positrons. Suitable corrections, which are discussed below, were made for the non-equivalence of the targets by determining the ionization losses.

Substances of high degree of purity were used—of the grade chemically pure for cryoscopy; where necessary, redistillation with a rectification column (45–65 theoretical stages) was carried out. The purity of the substances was monitored by measuring the refractive index (n_D) with an IRF-23 refractometer at a temperature held constant within 0.05°. The deviations of n_D from the published data at the given temperature did not exceed 0.00010. After filling, the targets were carefully de-aerated and evacuated.

Flat targets were used in some cases. The temperature during the measurements was 20–

25° C, this being ensured by circulating water in the cooling jacket of the solenoid.

4. MEASUREMENTS

The measurements were made with a beam of 155 MeV/c μ^+ mesons extracted with the aid of a system of focusing lenses and deflecting magnets ("μ-channel"[4]) from the JINR synchrocyclotron.

In most cases the time of registration of the decay on the AI-100 scale was $\sim 6\,\mu$sec. At a magnetic field intensity of 50.0 Oe, one period of the meson spin precession corresponded to twenty channels of the AI-100 (meson frequency). The precession of atomic muonium in the triplet state, which occurred at a frequency ~103 times larger (muonium frequency), was traced at the corresponding magnetic field intensity in the 18.9 and 4.9_4 nsec/channel ranges.

The standard exposure was 30–35 minutes. The number of μ signals during this time was 2×10^6 (~100 pulses/sec). The number of counts in one channel reached 3,000 pulses near the start of the decay curve (at an apparatus transmission of approximately 1/20). The random-coincidence background was 8–10%. Experiments in which the 18.9 and 4.9_4 nsec/channel ranges were used were made at maximum beam intensity (~2200 pulses/sec), in which case the background level was somewhat higher.

In each series of experiments, measurements were made of the asymmetry coefficient of μ–e decay in a target made of bromoform ($CHBr_3$), which was chosen as the standard. To determine the corrections for the non-equivalence of the targets, the ionization losses were used to determine the plot of the asymmetry coefficient against the target thickness (aluminum target) (Fig. 3), to which the obtained results were normalized for an identical recorded-positron energy spectrum.

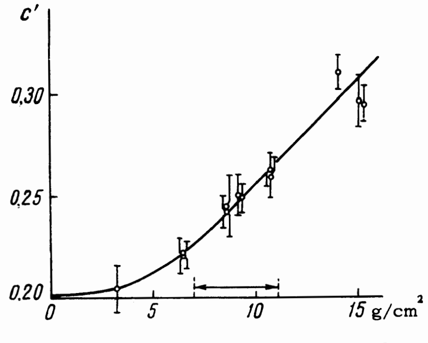

FIG. 3. Dependence of the asymmetry coefficient on the thickness of the absorbing substance. The arrow indicates the working dimensions of the target.

5. DATA REDUCTION AND CORRECTIONS

The obtained time spectra of μ^+ decay were reduced with an electronic computer using the equation

$$N(t) = N_0 e^{-t/\tau}[1 - c' \cos(2\pi t / T + \delta)] + B, \qquad (1)$$

where N is the number of counts at the instant of time t, τ is the lifetime of the μ^+ meson, T the period of the precession curve, δ the initial phase of the curve, due to the radiotechnical delay of the circuit and the geometry of the setup, and B is the background.

If the "zero time" corresponded to the eightieth AI-100 channel, then the channels 85–97 were used to measure the background, while channels 6–78 were used to measure the asymmetry coefficients. The remaining channels were not included in the data processing because of the nonlinearity of the recording system. The information extracted from the computer contained the values of N_0, c′, T, δ, the probable errors of these parameters obtained by the Monte Carlo method, and the distribution of the number of counts over the channels, corrected for the decay. We also determined the asymmetry coefficients corresponding to each half-period of the precession curve. A representative curve is shown in Fig. 4. With a typical number of 2×10^6 stopped μ^+ mesons in the target, the statistical accuracy of determining $\Delta c' = \pm 0.007$.

The obtained values of c′ were corrected for the energy spectrum of the emitted positrons (Fig. 3) and the contribution of the target wall material ($\leq 1\%$). Separate experiments that have shown that the correction for the difference in the radiation losses of the decay positrons, due to the different atomic numbers of the nuclei of the target material, is insignificant. The correction lies within the limits of the statistical errors of the experiment. The factor that takes into account the discreteness of the obtained spectrum differs from unity by an amount < 0.5%.

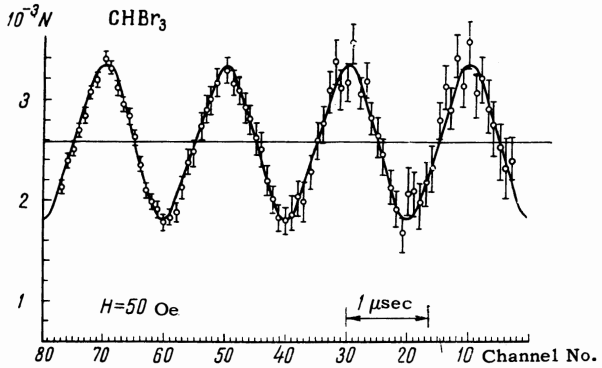

FIG. 4. Precession curve in bromoform ($CHBr_3$).

Repeated measurements (up to 2–5 times), which agreed within the limits of the statistical errors, were made for the majority of the individual substances. Mean-weighted values were obtained for them.

The corrected values of c′ contain a factor f, which takes into account the polarization of the μ^+-meson beam in the channel and the geometrical parameters of the recording telescopes. Using the absolute values of Bardon et al.[5] for $CHBr_3$, measured near the threshold of emission angle of the μ^+ mesons (c′ = 0.325 ± 0.015), we obtain for an infinitesimally thin layer of absorbing medium $f = 0.68_6 \pm 0.04_0$. Account of the geometry of the apparatus gives for the μ^+ meson beam polarization in the channel, at a momentum 155 MeV/c, a value P = 0.75 ± 0.04.

6. RESULTS AND CALCULATION OF THE REACTION RATE CONSTANTS

The obtained values of c′ are given in Tables I–III. Comparison with the data obtained by other authors[6, 7] shows agreement within the limits of experimental errors, with allowance for the polarization of the employed beam.

The rate constants of the chemical reaction between muonium and matter were calculated in accordance with a kinetic scheme which was analyzed in detail earlier.[1] The final expression relating the asymmetry coefficient in the angular distribution of the decay positrons at the meson frequency with the rate constants for the individual substance was obtained in an earlier communication:[2]

$$\frac{k_1[\mathrm{RH}]}{k_2[\mathrm{RH}]+k_5+k_4/A}=\frac{c'}{fc-c'},$$
$$A=2+\frac{k_4}{(k_1+k_2)[\mathrm{RH}]+2k_3[\mathrm{RH}]+k_5}. \qquad (2)$$

Here k_1 and k_2 are the rate constants for the formation of molecular and radical products, respectively, k_3 the rate constant for the triplet-singlet conversion, k_4 the rate constant for depolarization of muonium in the singlet state,[8] k_5 the rate constant of μ^+ meson decay, [RH] the concentration of the substance, c the theoretical maximum value of the asymmetry coefficient, c′ the experimental asymmetry coefficient corrected for the energy spectrum of the outgoing positrons and for the contribution of the wall material, and f a factor that takes into account the geometry of the apparatus and the polarization of the beam.

For solutions of different concentrations, Eq. (2) must be subjected to the following transformations —in place of k_1 [RH], for example, we substitute

Table I. Values of the asymmetry coefficients for several compounds and their solutions (in mol. %)

Substance	c′	Substance	c′
$CHBr_3$	0.223±0.008	$C_6H_6 - C_6H_{12}$ (29.0%)	0,059±0.007
C_6H_{12}	0.160±0.009	$- C_6H_{12}$ (60.5%)	0.108±0.007
CH_3OH	0,137±0.009	$- C_6H_{12}$ (90.3%)	0,141±0.008
C_8H_{18}	0,147±0.008		
$CHCl_3$	0.190±0,009	$CHCl_3$ — DPPH (0.050%)	0,195±0,009
C_6H_6	0.036±0,006	— DPPH (0.50%)	0,190±0.009
$C_6H_6 - CHBr_3$ (25.0%)	0,156±0.008	$CH_3OH - C_6H_{12}$ (10.0%)	0,153±0,009
$- CHBr_3$ (10.1%)	0.121±0.009	$- C_6H_{12}$ (20.0%)	0,155±0,009
$- CHBr_3$ (3.0%)	0.085±0.009		
		$C_6H_6 - CHCl_3$ (3.0%)	0,060±0.009
$CH_3OH - C_6H_6$ (50.3%)	0,058±0.007	$- CHCl_3$ (10.0%)	0.077±0.010
$- C_6H_6$ (20.0%)	0.085±0,008	$- CHCl_3$ (25.0%)	0.105±0,008
$- C_6H_6$ (10.0%)	0.102±0.007		
		C_6H_6 — DPPH (0,050%)	0,040±0.007
$C_8H_{18} - CHBr_3$ (4.9%)	0,160±0.007	— DPPH (0.50%)	0,070±0.007
$- CHBr_3$ (15.0%)	0.178±0,009	— DPPH (0.65%)	0,085±0.009

Table II. Values of the asymmetry coefficient for different field intensities

Substance	H, Oe	c′	Substance	H, Oe	c′
C_6H_{10}	50	0.113±0.009	C_6H_6	50	0.036±0,006
C_6H_{10}	271	0,116±0.008	C_6H_6	271	0.034±0.007
$CHBr_3$	50	0.223±0.008	Polystyrene	50	0.044±0.007
$CHBr_3$	271	0.219±0,009	Polystyrene	271	0,034±0.007

the expression $k_1'[RH]' + k_1''[RH]''$, etc. Binary mixtures are employed to make possible the use of the widely employed competing-acceptors method of chemical kinetics when the rates of the processes occurring in parallel are additive.

This is of importance, first, for an increase of the accuracy of the determination of the rate constants. Indeed, for $CHBr_3$ ($c' = 0.223 \pm 0.008$) we have $\Delta k_1 = {}^{+\infty}_{-60\%}$, whereas for C_8H_{18} ($c' = 0.147 \pm 0.008$) we have $\Delta k_1 = {}^{+18\%}_{-12\%}$. The use of the method of competing acceptors makes it possible to obtain a more accurate value for $CHBr_3$, $\Delta k_1 = {}^{+27\%}_{-19\%}$ (from the values of c′ for the mixtures of the components). Generally speaking, the accuracy can be increased to a value equal to the error of the most favorable case.[1] We note that for heterogeneous mixtures, where the contribution of the parallel reactions has been greatly reduced, or in the absence of chemical interactions, the dependence of c′ on the concentration of the components should be linear, whereas for the competing acceptors the analogous dependence is determined by the ratio of the rate constants of the components. A representative curve in this sense is that for C_6H_6—$CHBr_3$ (Fig. 5a), where $\Sigma k'/\Sigma k'' \sim 10$.

Second, measurement of c′ for an individual substance at the mesonic frequency makes it possible to determine only k_1, whereas the amount of muonium consumed in the formation of radical products with a rate constant k_3 is disclosed by the method of competing acceptors, a fact taken into account in the kinetic equations. This points to a way of establishing the mechanism of the occurring processes. Thus, for example, for the mixture C_6H_6—C_6H_{12} (Fig. 6d), taking only k_1 into account, the curve has the form shown by the dashed line, in contradiction to the experimental data. If we take into account, on the other hand, the formation of radical products upon "adhesion" of the atomic muonium to the benzene molecule, then the contradiction is quantitatively eliminated (Fig. 6d—solid curve), and furthermore $k_2 > k_1$. Kinetic investigations of the interactions of atomic hydrogen[9] confirmed this conclusion. This question is considered in greater detail below.

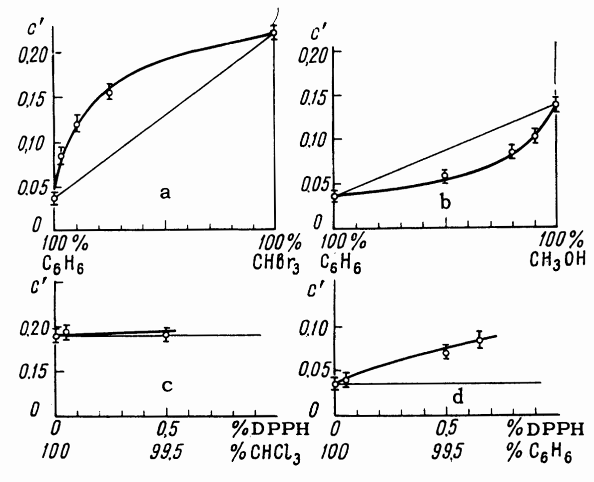

FIG. 5. Dependence of the asymmetry coefficient on the concentration of the components of the solution (in mole.%): a – CH_3OH – C_6H_{12}; b – C_6H_6 – $CHCl_3$; c – C_8H_{18} – $CHBr_3$; d – C_6H_6 – C_6H_{12}.

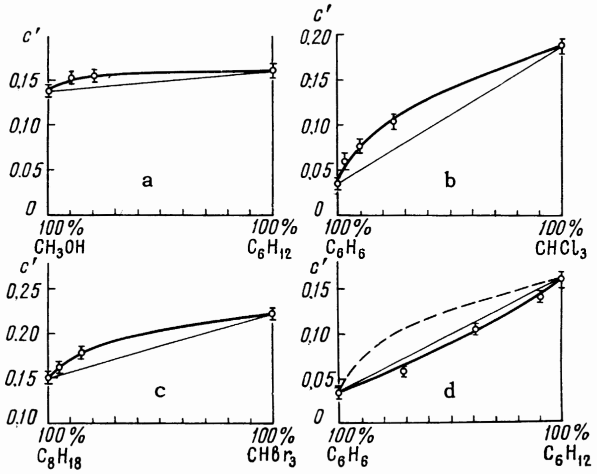

FIG. 6. Dependence of the asymmetry coefficient on the concentration of the components of the solution (in mol.%): a – C_6H_6 – $CHBr_3$; b – C_6H_6 – CH_3OH; c – $CHCl_3$ – DPPH; d – C_6H_6 – DPPH.

In checking the obtained values against one another, it is important to have several ways of determining k, that is, to have an overdetermined system. Table I lists the asymmetry coefficients for several mixtures (Figs. 5, 6) which are unified by the scheme shown in Fig. 7.

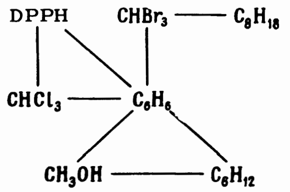

FIG. 7. Diagram of system of substances and their solutions.

The calculated rate constants of the corresponding muonium reactions are given in Table IV, which includes also the calculated data for certain individual substances. The self-consistency of the calculated values lies within 20–30%, which determines the final accuracy of the obtained quantities.

Table III. Values of the asymmetry coefficient for several compounds

Substance	c'	Substance	c'
H_2O	0,146±0.008	C_6H_5Cl	0.063±0.007
H_2O — Cu^{++} (1 mole /l)	0,150±0,009	C_6H_5Br	0,106±0.010
H_2O — Fe^{++} (0.5 mole /l)	0,135±0,008	$C_2H_4Cl_2$	0,152±0,010
H_2O — Fe^{+++} (0,5 mole /l)	0,132±0,008	CCl_4	0,237±0.012
C_8H_{18} ($H = 7{,}0$ Oe)	0.142±0.054	CH_2I_2	0,227±0,009
C_6H_6 ($H = 2{,}7$ Oe) *	0.005±0.006	Molybdenum	0.086±0.009
Tolan [$C_6H_5C \equiv CC_6H_5$] $H = 267$ Oe	0.031±0.013	Plexiglas	0.093±0.011
Anthracene [$C_{14}H_{10}$] $H = 267$ Oe	0.025±0.011		

*Muonium frequency.

Table IV. Values of the rate constants of chemical reactions of muonium with acceptors

Substance	k_1, l/mole-sec	k_2, l/mole-sec	k_{H+Ac}, l/mole-sec
C_6H_{12}	$1.2 \cdot 10^9 \begin{smallmatrix}+19\% \\ -15\%\end{smallmatrix}$	—	$4.0 \cdot 10^8$
CH_3OH	$2.7 \cdot 10^8 \begin{smallmatrix}+21\% \\ -16\%\end{smallmatrix}$	—	$9{,}0 \cdot 10^7$
C_8H_{18}	$1{,}1 \cdot 10^9 \begin{smallmatrix}+18\% \\ -12\%\end{smallmatrix}$	—	$3.7 \cdot 10^8$
$CHCl_3$	$5.0 \cdot 10^9 \begin{smallmatrix}+31\% \\ -24\%\end{smallmatrix}$	—	$1.7 \cdot 10^9$
C_6H_6	$3.4 \cdot 10^8 \begin{smallmatrix}+23\% \\ -18\%\end{smallmatrix}$	$1.3 \cdot 10^9 \begin{smallmatrix}+21\% \\ -18\%\end{smallmatrix}$	$5.5 \cdot 10^8$
$CHBr_3$	$1.6 \cdot 10^{10} \begin{smallmatrix}+27\% \\ -19\%\end{smallmatrix}$	—	$5.3 \cdot 10^9$
DPPH	$1.1 \cdot 10^{11} \pm 29\%$	—	$3.7 \cdot 10^{10}$
C_6H_{10}	$9.6 \cdot 10^8 \begin{smallmatrix}+25\% \\ -18\%\end{smallmatrix}$	$4.3 \cdot 10^8$	$4.6 \cdot 10^8$
C_6H_5Cl	$7.4 \cdot 10^8 \begin{smallmatrix}+30\% \\ -20\%\end{smallmatrix}$	$1.3 \cdot 10^9$	$6{,}8 \cdot 10^8$
C_6H_5Br	$1{,}7 \cdot 10^9 \begin{smallmatrix}+30\% \\ -20\%\end{smallmatrix}$	$1.3 \cdot 10^9$	$1{,}0 \cdot 10^9$
$C_2H_4Cl_2$	$7.0 \cdot 10^8 \begin{smallmatrix}+45\% \\ -34\%\end{smallmatrix}$	—	$2.3 \cdot 10^8$
CH_2J_2	$9.5 \cdot 10^{10} \begin{smallmatrix}+\infty \\ -85\%\end{smallmatrix}$	—	$3.2 \cdot 10^{10}$

In the fourth column are given the total reaction rate constants for atomic hydrogen, obtained from the collision theory with allowance for the differences of the masses of the atoms. The influence of the tunnel effect[10] has not been taken into account in this case, inasmuch as a noticeable contribution of the latter, in accordance with the estimates, takes place (at an activation-barrier width of 2 Å and at an activation energy of 1–4 kcal/mole) only at temperatures below 50–100° K. Comparison of the values obtained by recalculating the atomic hydrogen reactions with the published data[9, 11–16] (the accuracy of the rate constants of the reactions, as estimated from the cited errors in the determination of the activation energy of the processes, has a factor 10–100) shows satisfactory agreement within the limits of the experimental errors, and a much higher accuracy than can be attained by the muonium method.

7. DISCUSSION

As is well known,[11, 12] the main reaction in the interaction of atomic hydrogen with benzene is the formation of the radical product $C_6H_7\cdot$ (or $C_6H_6Mu\cdot$ for muonium). At the mesonic frequency this product cannot be observed but, as shown above, the method of competing acceptors yields values $k_1 = 3.4 \times 10^8$ and $k_2 = 1.3 \times 10^9$. The total value, recalculated for atomic hydrogen, agrees with that of Melville and Robb,[12] namely, 6×10^8. Interest is attached to the large value of k_1, since it is not determined in physico-chemical investigations, owing to the small yield of the molecular products. We note that k_1 includes different reactions of formation of molecular products—detachment, isotopic exchange, ring destruction, etc. It is also clear from the kinetic point of view that molecular and radical products can be produced only in parallel reactions. Indeed, the successive formation of radical products from molecular ones contradicts the rate-constant ratio, while the inverse leads to the formation of depolarized products.

Of obvious interest was the problem of experimentally observing radical products in benzene and other unsaturated compounds. We used the following methods: observation of precession at the muonium frequency (C_6H_6), dependence of the asymmetry coefficient on the magnetic field intensity[8] up to 271 Oe (C_6H_6, C_6H_{10}, $C_{14}H_{10}$—tolan, $C_{14}H_{10}$—anthracene, polystyrene), comparison of the decay curve (H = 0) and of the precession curves (C_6H_6). The latter method is based on the fact that at the chosen counter geometry the decay curve corresponds to the minima of the precession curve. Consequently, the presence of appreciable modulation at the muonium frequency should lead to a change in the position of the decay curve. In all cases (Tables II and III, Fig. 8) the expected effect is within the limits of the statistical errors.

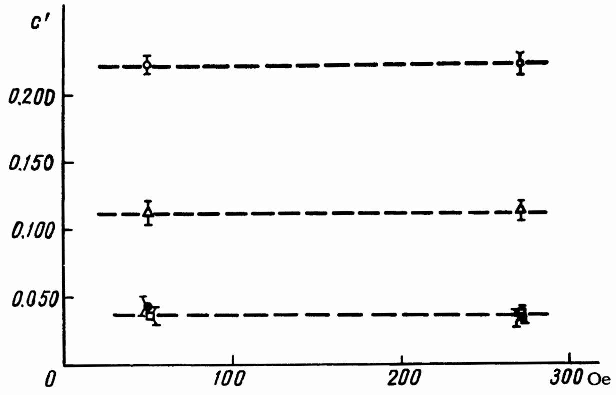

FIG. 8. Dependence of the asymmetry coefficient on the magnetic field intensity for several compounds: ○ – $CHBr_3$, □ – C_6H_6, △ – C_6H_{10}, ● – polystyrene.

It is quite obvious, however, that the method of competing acceptors indicates that a fast reaction of muonium consumption takes place. It can be assumed that in this case an important role is played by a mechanism which was theoretically analyzed for the joining of atomic hydrogen to a multiple bond.[16] The break in the interaction of the multiple-bond π electron spins, situated in a perpendicular plane relative to the spins of the σ electrons, leads to the rotation of the C–C bond, caused by electromagnetic factors, through an angle determined by the spatial structure of the molecules (for linear molecules—by 90°). Inasmuch as the orientation of the molecules in the medium is random, the average summary polarization is zero. It is interesting to note that in those cases when the rotation is excluded as a result of structural features (for example, triple bond), we can expect the absence of such a mechanism. In tolan, (Table III), however, the main contribution is apparently made by the interaction with the phenyl groups, which screen the triple bond. A similar analysis may be necessary to clarify the nature of the π complexes of unsaturated molecules.

Charpak et al.[17] and Buhler et al.[18] indicate that the asymmetry coefficient in polystyrene increases with increasing field intensity, whereas in our experiments (Fig. 8) there is no dependence on H. The resultant contradiction calls for further explanation. It can be noted, however, that in [17, 18] a procedure was used for measuring the asymmetry of the forward-backward in a longitudinal magnetic field, whereas in the present paper we used the statistically more reliable procedure of spin precession in a transverse magnetic field. Individual experiments with $CHBr_3$ (Fig. 8) have confirmed the correctness of the assumption that c′ is independent of the intensity of the magnetic field for saturated molecules. It is interesting to note the presence of precession at the muonium frequency in polystyrene at liquid-nitrogen temperature.[19] This is undoubtedly connected with the slowing down of the rate of the chemical reactions with decreasing temperature.

A study of the homological series of organic compounds (chloralkyls with different numbers of C–Cl bonds—Fig. 9, different halide alkyls—Fig. 10, halide-aromatic compounds—Fig. 11) indicate that the reactivity of substances per unit functional bond may be additive. The data obtained are insufficient for detailed calculations, but the persistent trend of the corresponding relationships is confirmed by the investigations of similar reactions of atomic hydrogen.

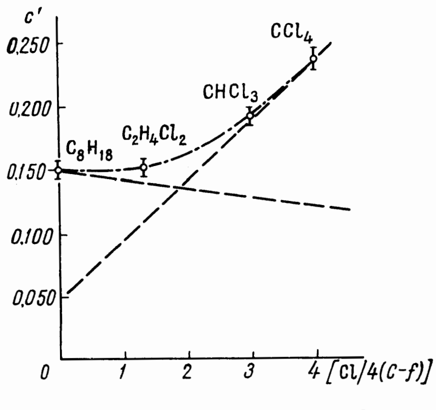

FIG. 9. Dependence of the coefficient of asymmetry on the ratio of the number of C-Cl bonds to all the heteroatomic bonds in the molecule.

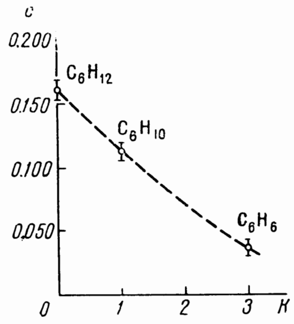

FIG. 10. Dependence of the asymmetry coefficient on the number of short bonds K in a six-member ring.

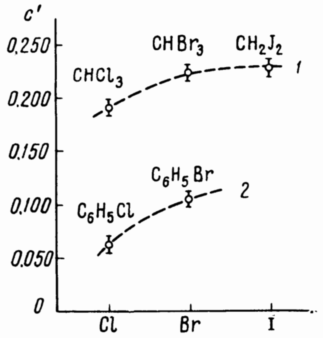

FIG. 11. Dependence of the coefficient of asymmetry on the nature of the halide in halide alkyls (curve 1) and halide benzenes (curve 2).

The high reaction rate of free radicals is essential for the problem of obtaining standard substances with a maximum asymmetry coefficient.[1] By way of an example we measured the asymmetry coefficients in solutions of the stable free radical diphenyl pycril hydrazil (DPPH) in C_6H_6 and $CHCl_3$ (Table I). The obtained value of k_1, being close to the value obtained from the number of collisions, confirms that the activation energy of the process is very small. According to calculation, at a DPPH concentration of 10 mole/1 in the solution, c′ should differ from the maximum value by not more than 0.002. The preparation of such concentrated solutions, however, entails certain difficulties. As shown by the data of Table III, the use of multiply substituted halide alkyls gives practically similar results.

It is of interest to investigate the chemical reactions of muonium with inorganic ions of variable valence in aqueous solutions, inasmuch as a specific feature of these interactions is the oxidation-reduction process of electron transfer. The value of c′ obtained directly for the solvent corresponds to a rate constant $k_1 = 1.3 \times 10^8$, which apparently corresponds to the sum of the isotopic exchange reactions, formation of MuH molecules, and possibly to the hydration of μ^+ meson with formation of the MuH_2O^+ ion, which is similar to the hydroxonium ion. It is not excluded that an appreciable role is played by formation of associations with bonds of the hydrogen type with compensated electron spins.

The high rate of muonium interaction with the solvent leads to a relatively small contribution of the reactions of ions of variable valence (Table III) and to considerable errors in the determination of the reaction rate constants. Assuming single interaction of the muonium with a transfer of an electron to the Cu^{++} ion, the rate constant of this process was found to be 10^8–10^9 (radiation-chemistry investigations of a similar reaction, when suitably recalculated, lead to a value 3.2×10^8[20]). A special role is played by reactions of ions with unpaired electrons, since the contribution of the conversion reaction is quite large for them. In this case it is possible to solve to inverse problem—calculate k_3 from known values of k_1 for the ions Fe^{++} and Fe^{+++}.[20] In spite of the appreciable errors, values of the same order of magnitude were obtained, 4×10^9 and 5×10^9, respectively. We note that k_3 should also be of the same order for DPPH with one unpaired electron, but since $k_1 \gg k_3$ the contribution of the conversion reaction is negligible.

More detailed investigations will apparently make it possible to find the connection between the rate constant of the conversion reaction and the energy parameters of the electron bond in different compounds.

One of the possible ways of identifying the products obtained when muonium interacts with matter is to study the spin states of nuclei in molecules.[2] The precession in a magnetic field which is not sufficient ($H < H''_{\text{crit}}$) to break the bond of the magnetic moments of the meson and of the nearest nucleus, should be determined by the summary magnetic moment and spin of the system. In particular, for the MuH molecule at sufficiently low magnetic field intensity, the asymmetry coefficient should be twice as small and the precession frequency approximately one-third the corresponding values for the precession of the μ^+ meson. The attempt made to find the precession of the meson-proton system in the MuH molecule (the product of interaction of muonium with octane C_8H_{18}) in a field of 7.0 Oe has shown (Table III) that the precession corresponds to the mesic frequency, and the asymmetry coefficient has undergone no changes within the limits of experimental errors. It follows therefore that $H''_{\text{crit}} < 7$ Oe. Searches should be continued in the region of smaller magnetic fields.

8. CONCLUSIONS

The obtained experimental material shows quantitatively the similarity of the reactions of atomic hydrogen and muonium with substances of different classes. By the same token, the feasibility is confirmed of a new physical method for investigating reactions of atomic hydrogen when the latter is simulated by muonium. The advantages of the muonium method are its universality with high measurement accuracy and the possibility of disclosing subtle features of the spin states of the intermediate product. Investigations of reactions in a condensed medium will make it possible to avoid introducing any premises for the transition from the gas phase to other phases.

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