TABLE 1

Product yields from the triboelectrical discharge decomposition of hydrocarbons and acetone*

Substrate	Pressure (Torr)	Relative gas chromatogram peak areas of products										
		Me_2Hg	C_2H_2	C_2H_4	C_2H_6	H_2	C_3H_8	C_3H_6	CH_4	C_4†	MeHgEt	CO
CH_4	10	128	60	52	45	29	17	2	—	—	—	—
C_3H_8	10	55	60	32	112	12	—	50	145	35	11	—
CH_3COCH_3	12	621	—	—	137	—	23	27	107	45	—	814
C_2H_4	11	171	2014	—	208	62	72	147	333	—	191	—
$\{H_2$ C_2H_4	8.3 6.6	40	396	—	130	—	42	21	—	17	—	—

*Conversions ranged from 5 to 30%.
†C_4-hydrocarbons.

the table, of which the synthesis of ammonia and hydrazine from a 3:1 mixture of N_2 and H_2 is noteworthy.

Similar reactions could be brought about by bubbling the appropriate gases through a pool of mercury.

The mechanisms of these reactions are obviously complex. The processes include electrical breakdown and direct and sensitized photolysis.

These phenomena have implications for gas phase kinetic studies. It is possible to produce spurious reactions in the Toepler pump and in other equipment where moving mercury surfaces are in contact with glass or gas materials. This possibility was checked and from hydrocarbons and acetone, we would indeed produce noncondensable gases on extensive pumping.

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1. J. A. Medley. Brit. J. Appl. Phys. Supp. 2, **28** (1953). W. R. Harper. Advan. Phys. **6**, 365 (1957).
2. L. J. Schoen. Can. J. Phys. **38**, 967 (1960).
3. K. Ikenoue and Y. Sasada. Mem. Defense Acad. Jap. **II**, 49 (1962); **II**, 57 (1962).
4. J. L. Sherman, C. E. Cardwell, D. Q. Lamb, Jr., and C. E. Mandeville. Bull. Amer. Phys. Soc. **11**, 77 (1966).
5. G. L. Dybwad and C. E. Mandeville. Phys. Rev. **161**, 527 (1967).
6. G. L. Dybwad. J. Appl. Phys. **40**, 4977 (1969).
7. A. Wolf. A History of Science, Technology and Philosophy in the 16th and 17th centuries. MacMillan, New York. 1935. p. 303.
8. Fra. Hauksbee. Phil. Trans. Roy. Soc. London, **24**, 2130 (1705). I. Newton Optics, or A treatise of the reflections, refractions, inflection and colours of light. 2nd ed. (1718) Qu. 8.

Kinetics of the exchange reaction of dimethylarsenic deuteride with diethylarsine

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The exchange reaction $(CH_3)_2AsD + (C_2H_5)_2AsH \rightleftharpoons (CH_3)_2AsH + (C_2H_5)_2AsD$ can be monitored by conventional nuclear magnetic resonance spectroscopy. The equilibrium constant in diethyl ether-d_{10} solution is 1.2 ± 0.1 and the rate constant for the forward reaction is $4.95 \pm 0.25 \times 10^{-5}$ l mole^{-1} s^{-1} at 35°. Dimethylarsine exchanges rapidly with methanol-d_4 and bis(trifluoromethyl)arsinic deuteride.

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Knowledge of the rate of exchange of secondary arsine protons, as in reaction 1, was important in determining the mechanism of the addition of secondary arsines to hexafluorobutyne-2,

$$[1]\quad (CH_3)_2AsD + (C_2H_5)_2AsH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (CH_3)_2AsH + (C_2H_5)_2AsD$$

because the distribution of the deuterium label in the products of the competitive reaction described by reaction 2, would give mechanistic information

$$[2]\quad \left.\begin{array}{l}(CH_3)_2AsD\\ (C_2H_5)_2AsH\end{array}\right\} + CF_3C{\equiv}CCF_3 \rightarrow \begin{array}{l}(CH_3)_2AsC(CF_3){=}C(CF_3)\binom{D}{H}\\ (C_2H_5)_2AsC(CF_3){=}C(CF_3)\binom{H}{D}\end{array}$$

only if no significant exchange occurred between the reactants and/or products (1).

Proton transfer reactions have been studied using a wide variety of methods (2), including specialized fast reaction techniques (3). However, reaction 1 was slow enough to be followed by simple integration of the nuclear magnetic resonance (n.m.r.) spectrum of the reaction mixture.

Experimental and Results

Starting Materials and Techniques

A vacuum system was used for the manipulation of volatile substances. Nuclear magnetic resonance spectra were run on Varian A 60 (^{1}H spectra in p.p.m. downfield from external TMS), and HA 100 (^{19}F spectra in p.p.m. upfield from internal $CFCl_3$) spectrometers. Methanol-d_4 (99.9%), diethyl ether-d_{10}, deuterium chloride, and D_2O were purchased from Merck, Sharp and Dohme of Canada Ltd. Bis(trifluoromethyl)-arsine was prepared from tetrakis(trifluoromethyl)diarsine by reacting this with hydrogen chloride in the presence of mercury (4). The ^{1}H n.m.r. spectrum showed a septet centered at 5.08 p.p.m. (J_{CF_3-H} = 9.2 Hz) and the ^{19}F n.m.r. spectrum a doublet centered at 42.3 p.p.m. Bis(trifluoromethyl)arsenic deuteride was similarly prepared using deuterium chloride. The ^{1}H n.m.r. spectrum of the product indicated that some hydride was present. The material was shaken with D_2O for two weeks to yield pure bis(trifluoromethyl)arsenic deuteride. The gas phase infrared spectrum of the deuteride run on a Perkin–Elmer 457 instrument showed main bands at 1548 m, 1190 s, 1168 s, 1120 s, 734 cm^{-1}. Dimethylarsenic deuteride and diethylarsine were prepared as previously described (1).

Proton Exchange Reactions and Kinetics

Weighed portions of materials whose exchange was to be followed, plus a measured amount of solvent when used, were sealed in n.m.r. tubes and kept frozen until they were to be studied. The tubes were quickly warmed to room temperature and placed immediately in the n.m.r. spectrometer. Care was taken to isolate the starting materials with a layer of solvent, to try to prevent any unnecessary exchange before the mixing was complete.

In a typical experiment, 0.118 g of diethylarsine, then diethyl ether-d_{10}, and finally 0.036 g of dimethylarsenic deuteride were sealed in an n.m.r. tube. Upon quickly warming the tube to 35°, the exchange was followed by integrating over the methyl peaks of dimethylarsine and dimethylarsenic deuteride. Figure 1 shows typical spectra in this region run at a sweep width of 50 c.p.s. The following results were found.

t(s)*	Concentration of $(CH_3)_2AsD$ (moles/l)
3 600†	0.458
3 765	0.459
3 870	0.452
7 935	0.337
8 100	0.341
8 220	0.331
10 080	0.303
10 260	0.301
10 425	0.306
11 940	0.271
12 030	0.280
12 120	0.278

*t = 0 is arbitrary.

†Previous to this time the methyl peaks of the hydride and deuteride were not separated well enough for reliable integration.

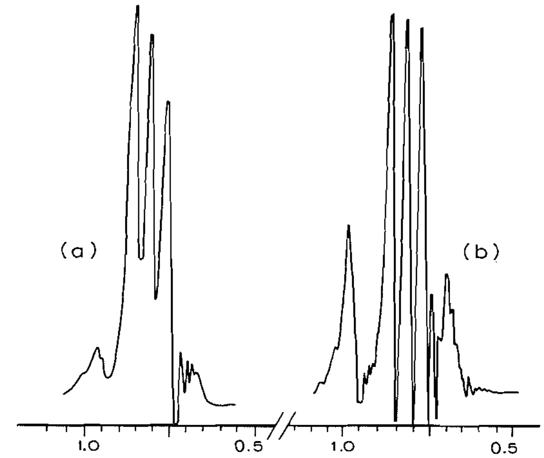


FIG. 1. ^{1}H n.m.r. spectra of the CH_3 region in mixtures of $(CH_3)_2AsH$ and $(CH_3)_2AsD$. (*a*) Mainly $(CH_3)_2AsD$, (*b*) a higher proportion of $(CH_3)_2AsH$.

The following reaction scheme yields a kinetic rate law which corresponds with the experimental results

$$[3] \qquad AD + BH \xrightarrow{k_1} AH + BD$$

$$[4] \qquad AH + BD \xrightarrow{k_{-1}} AD + BH$$

If the following abbreviations for concentrations are made: at t = 0, [AD] = a and [BH] = b; at $t = t$, [AH] = x = [BD] and [AD] = $a - x$; the rate law from reactions 3 and 4 is

$$[5] \qquad dx/dt = k_1(a - x)(b - x) - k_{-1}x^2$$

TABLE 1

The rate and equilibrium constants for the proton exchange reactions*

Reactant A	Concentration of A (mole/l)	Reactant B	Concentration of B (mole/l)	Solvent	K	k_1
$(CH_3)_2AsD$	4.32	$(C_2H_5)_2AsH$	5.95	Neat	1.315	—
$(CH_3)_2AsD$	3.74	$(C_2H_5)_2AsH$	6.24	Neat	1.335	5.9×10^{-5}
$(CH_3)_2AsD$	1.12	$(C_2H_5)_2AsH$	2.43	$(C_2D_5)_2O$	1.1	4.7×10^{-5}
$(CH_3)_2AsD$	0.852	$(C_2H_5)_2AsH$	2.19	$(C_2D_5)_2O$	1.365	5.2×10^{-5}
$(CH_3)_2AsD$	0.275	$(C_2H_5)_2AsH$	2.71	$(C_2D_5)_2O$	†	†
$(CH_3)_2AsH$	2.46	$(CF_3)_2AsD$	1.76	$(C_2D_5)_2O$	0.28	‡
$(CH_3)_2AsH$	0.187	$(CF_3)_2AsD$	0.450	$(C_2D_5)_2O$	0.36	‡

*The reaction temperature is ~ 35°.

†Due to the small amount of dimethylarsenic deuteride used, the diethylarsine peaks overlapped seriously in the n.m.r. spectrum.

‡Too fast to measure.

Solving eq. 5 and using the equilibrium constant, $K = k_1/k_{-1}$, gives the result

$$[6] \quad k_{-1}t = \frac{1}{\sqrt{-q}} \ln\left(\frac{2cx + d - \sqrt{-q}}{2cx + d + \sqrt{-q}}\right)$$

where $q = 4Kab(K - 1) - K^2(a + b)^2$, $c = (K - 1)$, and $d = -K(a + b)$. Plotting t against $\ln(2cx + d - \sqrt{-q})/(2cx + d + \sqrt{-q})$ gives a straight line as seen in Fig. 2. From the slope, k_{-1}, and thus k_1, can be determined from a knowledge of the value of K.

A number of exchange reactions of dimethylarsine or dimethylarsenic deuteride were monitored by n.m.r., as described above, and the results are summarized in Table 1.

Discussion

Of the different proton exchanges of hydrides with dimethylarsine investigated (Table 1), only the reaction described by eq. 1 could be studied kinetically. The proton exchange of the arsines corresponds with a rate law [5] based on the mechanism outlined in reactions 3 and 4 whose solution is eq. 6. The rate constants (k_1) for the exchanges done neat and in diethyl ether-d_{10} solvent, are 5.9×10^{-5} and $4.95 \pm 0.25 \times 10^{-5}$ l mole^{-1} s^{-1} at 35°. The equilibrium constants are 1.335 ± 0.020 and 1.2 ± 0.1, respectively.

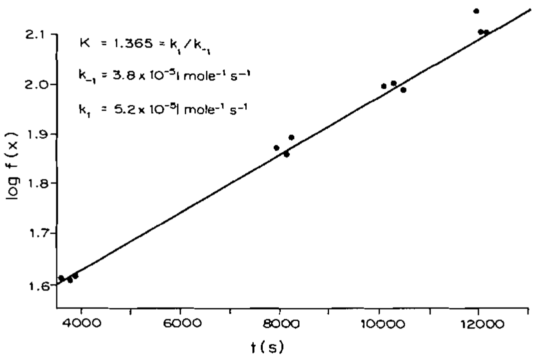


FIG. 2. Plot of $\log f(x)$ against time (eq. 6) for the reaction of $(CH_3)_2AsD$ with $(C_2H_5)_2AsH$ in $(C_2D_5)_2O$ solution.

The range of concentrations that could be satisfactorily used for these rate studies was very small, as will now be explained. Since the equilibrium in reaction 1 was to the right, it was desirable to study the exchange from the left side to increase the relative difference in concentrations between the dimethylarsenic deuteride and hydride monitored during the reaction. At high dimethylarsenic deuteride concentrations, relative to diethylarsine, there were too few protons exchanged at equilibrium to make integration practical. Consequently, the diethylarsine concentration had to be the greater of the two to give satisfactory results. Due to the overlap of small diethylarsine peaks in the n.m.r. spectra, with the methyl peaks for dimethylarsine, dimethylarsenic deuteride could not be less than 1/3 of the concentration of diethylarsine. If it were less than this, analysis was impossible as is seen in the last diethylarsine example in Table 1. The optimal relative concentrations were used for the rate studies in the three successfully analyzed experiments. It was found when the concentrations were changed absolutely and not relatively, these exchanges obeyed the same rate law and had similar rate constants. The exchange of these hydrides was slightly faster when done neat than when done in diethyl ether-d_{10}.

The exchange rate of bis(trifluoromethyl)-arsenic deuteride with dimethylarsine was studied in the hope of finding another slow exchange system that could be used in the competitive addition to hexafluorobutyne-2. (*c.f.* reaction 2) The rate of exchange in reaction 7 was found to be too fast to measure by n.m.r. integration techniques. Calculation of the equilibrium constant, 0.32 ± 0.06 in diethyl ether-d_{10} at 35° was possible, however. Consequently these hydrides are

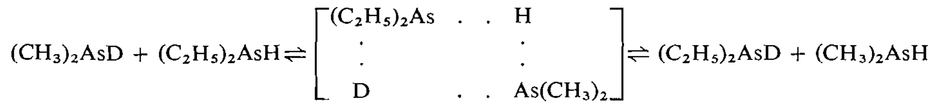
$$[7]\quad (CF_3)_2AsD + Me_2AsH \rightleftharpoons (CF_3)_2AsH + Me_2AsD$$

unsuitable for a competitive addition reaction, as they would exchange protons to a significant extent before addition to the acetylene occurred.

Dimethylarsine adds to hexafluorobutyne-2 in methanol solvent much faster than in ether and the product is 100% *trans* isomer (1), when the reaction is carried out in methanol-d_4 the 1:1 adduct is 85% deuterated (5). However, we have now found a fast exchange takes place between dimethylarsine and methanol-d_4 so that an interpretation of the deuterium content of the adduct in terms of the mechanism of the addition reaction is not possible.

The mechanism involved in these exchanges is open to speculation. An ionic or four-centered mechanism can meet the kinetic requirements. Meiboom and co-workers (6, 7) have indicated that the water–methanol proton transfer is non-ionic in a neutral solution, but ionic when traces of bases or acids are present. At 25° the rate of the non-ionic process ($k_1 \sim 10^0$ l mole^{-1} s^{-1}) is much slower than the trace acid or base induced ionic process ($k_1 \sim 10^6$ l mole^{-1} s^{-1}). It is possible that the arsines are strong enough bases to promote an ionic exchange between themselves and methanol. However, the slow rate for the dimethylarsenic deuteride – diethylarsine exchange ($\sim 10^{-3}$ l mole^{-1} s^{-1}) seems to be against an ionic mechanism. Thus a four-centered mechanism could very well be the main path for the arsine exchange mechanism as depicted in reaction 8. This 4-center mechanism is favored by

[8]



$$(CH_3)_2AsD + (C_2H_5)_2AsH \rightleftharpoons \begin{bmatrix} (C_2H_5)_2As & \cdots & H \\ \vdots & & \vdots \\ D & \cdots & As(CH_3)_2 \end{bmatrix} \rightleftharpoons (C_2H_5)_2AsD + (CH_3)_2AsH$$

Gold and Satchell (2) for amine proton transfers, as well as by other authors for various related proton exchanges such as the tin hydride – tin deuteride exchange (8).

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1. W. R. Cullen and W. R. Leeder. Can. J. Chem. **47**, 2137 (1969).
2. V. Gold and D. P. N. Satchell. Quart. Rev. **9**, 51 (1955).
3. E. F. Caldin. Fast reactions in solution. Blackwell Scientific Publications, Oxford. 1964.
4. W. R. Cullen. Can. J. Chem. **39**, 1855 (1961).
5. W. R. Leeder. Ph.D. thesis. University of British Columbia, Vancouver 8, B.C. 1970.
6. Z. Luz, D. Gill, and S. Meiboom. J. Chem. Phys. **30**, 1540 (1959).
7. E. Grunwald, C. F. Jumper, and S. Meiboom. J. Amer. Chem. Soc. **81**, 4664 (1962).
8. W. P. Neumann and R. Sommer. Angew. Chem. Internat. Ed. **2**, 517 (1963).

Concerning rhenium nitrogen fluoride and technetium nitrogen fluoride

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We have shown that the reported (1) X-ray powder pattern of "ReNF" is that of NH_4ReO_4 and we suggest that the X-ray powder pattern of "TcNF" is that of $(NH_4)_2TcF_6$. In light of these results we suggest that the existence of the discrete phases ReNF and TcNF has not been proven.

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Introduction

La Valle *et al.* (1) have reported the existence of the compounds ReNF and TcNF which might be expected to have similarities to ZrNF, and ThNF (2). Apart from analytical data and X-ray powder results, no physical properties were reported. It became apparent as a result of our experiments that some of the data reported by La Valle *et al.* have been misinterpreted. We were able to prepare a black solid by the method

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