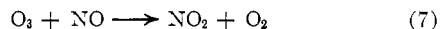
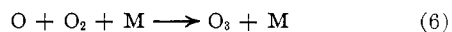
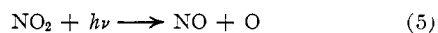


The lack of an effect on the initial rate of thermal oxidation due to the photolysis of nitrogen dioxide can be explained in terms of reactions 5-7.



The rapid rate of reaction 6¹⁷ is sufficient to convert all the oxygen atoms formed in reaction 5 to ozone. However, the rate of reaction 7 is sufficiently fast¹⁸ to remove

(16) H. W. Ford and N. Endow, *J. Chem. Phys.*, **27**, 1277 (1957).

(17) $k_6(\text{O}_2)(\text{M})$ is equal to $2.4 \times 10^4 \text{ sec.}^{-1}$ at 25°, in air at one atmosphere pressure: S. W. Benson and A. E. Axworthy, Jr., *ibid.*, **26**, 1718 (1957).

(18) k_7 is equal to $1.17 \times 10^{11} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ at 25°: H. S. Johnston and H. J. Crosby, *ibid.*, **22**, 689 (1954).

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

Microwave Absorption and Molecular Structure in Liquids. LII. Charge-Transfer Complexes^{1,2}

By JAMES E. ANDERSON³ AND CHARLES P. SMYTH

RECEIVED MAY 27, 1963

Measurements of the dielectric constant and loss of five charge-transfer systems have been carried out at various wave lengths between 1.25 and 40 cm. Dilute solutions of iodine in benzene and *p*-dioxane gave extremely small relaxation times, which are attributed to a rapid exchange mechanism. The kinetics of this mechanism are discussed and related to relaxation behavior. Triethylamine, tributylamine, and triphenylamine complexes with 1,3,5-trinitrobenzene were measured in dilute *p*-dioxane solution at 35°. Relaxation studies indicate that the triethylamine and tributylamine complexes are stable and dipolar. No evidence of a dipolar molecular complex between triphenylamine and 1,3,5-trinitrobenzene was observed. The possibility of different types of complexes is discussed.

Introduction

The recent literature contains a number of studies of charge-transfer complexes. On the basis of low frequency (static) dielectric measurements, the "apparent dipole moments" of many of these complexes have been determined.⁴ The common usage of the term dipole moment implies some sort of polar species which orients in the applied field. In certain charge-transfer systems, the existence of such a polar species has not yet been unambiguously demonstrated.

Atomic, electronic, and orientational terms may contribute to the observed static polarization of a liquid. Only molecules having permanent dipole moments possess an orientation polarization, while both polar and nonpolar molecules have atomic and electronic polarization. A dispersion associated with the atomic and electronic terms is manifest in the familiar infrared, visible, and ultraviolet absorption. For simple polar molecules in the liquid state, the dispersion region connected with orientation polarization occurs at microwave frequencies. For this reason, the presence or absence of a true polar species in a liquid system may be established through dielectric measurements in this frequency range.

Experimental

Purification of Materials.—U.S.P. resublimed iodine, obtained from the Baker and Adamson Co., was used without further purification. Reagent benzene and *p*-dioxane were purified by refluxing overnight above sodium and then distilled. The refractive indices, n_D^{20} , were 1.50084 and 1.42259, respectively. Triethylamine, obtained from Matheson, Coleman and Bell, was

purified by distillation; n_D^{20} 1.39958. Tributylamine was obtained from the Eastman Kodak Co. and was distilled under vacuum; n_D^{20} 1.42898. Triphenylamine was obtained from the Eastman Kodak Co. and was used without further purification; m.p. 125.0-125.6°.

ozone quantitatively from the system with the resultant formation of an equivalent amount of nitrogen dioxide. Thus, under the conditions of our experiments, no effect would be expected.

In conclusion, the results of this investigation are consistent with the generally accepted mechanism¹² for the thermal oxidation of nitric oxide as derived from studies²⁻⁵ carried out at much higher concentrations of nitric oxide. In addition it has been found that there is no effect on the thermal oxidation rate due to either (a) the addition of several olefins or (b) the photolysis of the product nitrogen dioxide.

Acknowledgment.—The authors wish to acknowledge the valuable assistance of Jerome Zemla in obtaining the data and preparing the manuscript.

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Treatment of Data and Experimental Results.—The experimental data for the iodine-benzene and iodine-*p*-dioxane complexes were treated by a modification of the method previously described.⁵ The equilibrium constant for each system⁶ was used to calculate the mole fraction of complex in each of six solutions. The slopes a' and a'' for each frequency were then calculated on the basis of change in dielectric constant and dielectric loss with mole fraction of complex. Since the dielectric loss is concerned only with the polar species present, this correction was necessary to account for the appreciable amount of noncomplexed, nonpolar iodine present in the system. The data are shown in Table I. The two-component systems of triethylamine, tributylamine, triphenylamine, and 1,3,5-trinitrobenzene in dilute *p*-dioxane solution were treated in the usual manner.⁵ Five solutions and the solvent were measured in each determination. Triethylamine, tributylamine, and triphenylamine were each mixed with 1,3,5-trinitrobenzene in dilute dioxane solution. Each tertiary solution was made up keeping the particular amine and trinitrobenzene in a 1:1 mole ratio. The a' and a'' slopes were then determined by plotting the dielectric constant and loss vs. mole fraction of a 1:1 complex. The data and results are presented in Tables II and III.

Apparatus.—The apparatus and measuring techniques have been described in previous papers.⁷⁻¹⁰

Discussion of Experimental Results

Complexes of Iodine.—Apparent dipole moments for iodine in nonpolar organic solvents have been reported by many observers.⁴ Fairbrother¹¹ has determined apparent moments of 1.3 and 0.6 D. for iodine in *p*-dioxane and benzene, respectively. Owing to the geom-

(5) A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly, and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 3447 (1950).

(6) G. Briegleb, ref. 4, pp. 124-125.

(7) W. M. Heston, Jr., E. J. Hennelly, and C. P. Smyth, *J. Am. Chem. Soc.*, **70**, 4093 (1948).

(8) H. L. Laquer and C. P. Smyth, *ibid.*, **70**, 4097 (1948).

(9) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly, and C. P. Smyth, *ibid.*, **72**, 3443 (1950).

(10) D. A. Pitt and C. P. Smyth, *J. Phys. Chem.*, **63**, 582 (1959).

(11) F. Fairbrother, *J. Chem. Soc.*, 1051 (1948).

(1) This research was supported by the National Science Foundation.
(2) This paper represents part of the work submitted by J. E. Anderson to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) American Machine and Foundry Fellow, 1961-1962; National Science Foundation Cooperative Fellow, 1962-1963; National Science Foundation Summer Fellow, 1963.

(4) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961, pp. 13-20.

TABLE I

SLOPES FOR THE DEPENDENCE OF THE DIELECTRIC CONSTANT AND LOSS UPON MOLE FRACTION OF COMPLEXED IODINE AT 25° AND CALCULATED RELAXATION TIMES

Solvent	a_0	a' (1.25 cm.)	a'' (1.25 cm.)	$\tau \times 10^{12}$ sec.
Benzene	2.663	2.564	0.192	3.4
Dioxane	3.847	3.617	0.473	3.2

TABLE II

SLOPES OF THE DIELECTRIC CONSTANT AND LOSS IN DILUTE *p*-DIOXANE AT 35°

Wave length, cm.	a'	a''
Trinitrobenzene (0-0.0348) ^a		
57500	1.28	
3.22	1.17	ca. 0
1.26	1.21	ca. 0
Triethylamine (0-0.0678)		
57500	0.340	
3.22	.198	0.242
1.26	-.245	0.246
Triethylamine-trinitrobenzene (0-0.0736)		
57500	2.32	
40	2.27	0.233
10	1.94	.475
3.22	1.37	.264
1.26	1.30	.130
Tributylamine (0-0.0333)		
57500	0.333	
3.22	-.128	0.300
1.25	-.276	0.144
Tributylamine-trinitrobenzene (0-0.0423)		
57500	2.19	
40	2.19	0.254
25	1.95	.359
10	1.69	.482
3.22	1.27	.354
1.25	1.13	.135
Triphenylamine (0-0.0390)		
57500	1.93	
3.22	2.07	0.05
1.25	1.97	0.08
Triphenylamine-trinitrobenzene (0-0.0395)		
57500	3.16	
3.22	3.19	0.06
1.25	2.96	0.08

^a Concentration range of solute shown in parentheses.

TABLE III

RELAXATION TIMES ($\times 10^{12}$ SEC.) FOR AMINES AND AMINE-TRINITROBENZENE COMPLEXES IN DILUTE DIOXANE SOLUTION AT 35°

Triethylamine	11
Triethylamine-trinitrobenzene	53
Tributylamine	30
Tributylamine-trinitrobenzene ^a	75

^a Obtained by separation of data in terms of two relaxation times.

etry of the iodine, benzene, and *p*-dioxane molecules, it is hard to envision a 1:1 complex between iodine and solvent whose structure would not possess a finite moment. On the other hand, the characteristic profound changes in the infrared, visible, and ultraviolet spectrum of a donor-acceptor system from the spectra of its constituents should appear as marked differences in atomic and electronic polarization. Thus, the static dielectric behavior of these iodine complexes may be

explained either by a stable polar molecular complex orienting in the applied field or by changes in the atomic and electronic polarization of the system arising from interactions between donor and acceptor.

Dielectric measurements of the systems iodine-benzene and iodine-*p*-dioxane were made at 575 m. and 1.25 cm. wave lengths. The data indicate an extremely high frequency dispersion region, but are insufficient to determine the size and shape of the curve. On the assumption of Debye behavior, relaxation times of 3×10^{-12} sec. were calculated, much less than would be expected for a stable polar complex under similar conditions. These results are in close agreement with those of Nederbragt and Pelle,¹² who studied the iodine-mesitylene system. Using the assumption of Debye behavior, these authors calculated a relaxation time 4×10^{-12} sec., which they interpreted in terms of a rapid exchange between polar molecular complexes and their nonpolar constituents. In view of the small stabilization energies of 1.3 and 3.5 kcal./mole¹³ for the iodine-benzene and iodine-*p*-dioxane complexes, such an explanation is extremely plausible if it can be shown that an exchange mechanism of this sort will lead to an unusually small relaxation time.

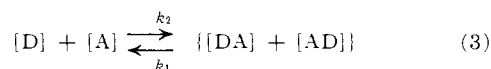
Effect of an Exchange Mechanism on Dielectric Relaxation.—Fröhlich¹⁴ has considered a simple model for relaxation, that of a jump process between two possible dipole positions aligned parallel and antiparallel to the external field direction. When a polar liquid is at equilibrium in an external field, there will be a larger number of molecules whose moment vectors make an angle $\theta = 0$ with the external field than those which make an angle $\theta = \pi$. Let [DA] represent the mole fraction of polar complexes with moment vectors in the $\theta = 0$ direction, and [AD] the mole fraction of complexes with moments in the $\theta = \pi$ direction. Complexes in [DA] pass into [AD] with rate constant k_4 , and [AD] complexes pass into [DA] with rate constant k_5 . Each of these rate constants may be expressed in terms of a contribution due to the field, and another due to an intermolecular energy barrier to rotation

$$k_4 = C \exp(-\Delta H/kT) \exp(-\mu F/kT) \quad (1)$$

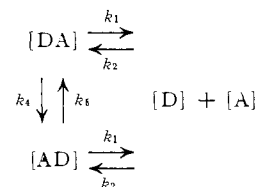
$$k_5 = C \exp(-\Delta H/kT) \exp(+\mu F/kT) \quad (2)$$

In eq. 1 and 2, C is a constant factor of the system, ΔH is the barrier to rotation, μ is the molecular dipole moment, k is the Boltzmann constant, and T the absolute temperature. It is obvious that if no external field is applied, $k_4 = k_5 = k_3 = C \exp(-\Delta H/kT)$.

The polar complexes are assumed to be in equilibrium with their nonpolar constituents through the relation



[D] and [A] represent the mole fractions of "free" donor and acceptor molecules, respectively. At experimental field strengths, the presence of an electric field will have no effect on this equilibrium. These two simultaneous equilibria make up the reaction scheme



The following rate equations apply to equilibrium in the

(12) G. W. Nederbragt and J. Pelle, *Mol. Phys.*, **1**, 97 (1959).

(13) G. Briegleb, ref. 4, p. 23.

(14) H. Fröhlich, "Theory of Dielectrics," Clarendon Press, Oxford, 1958, p. 67 ff.

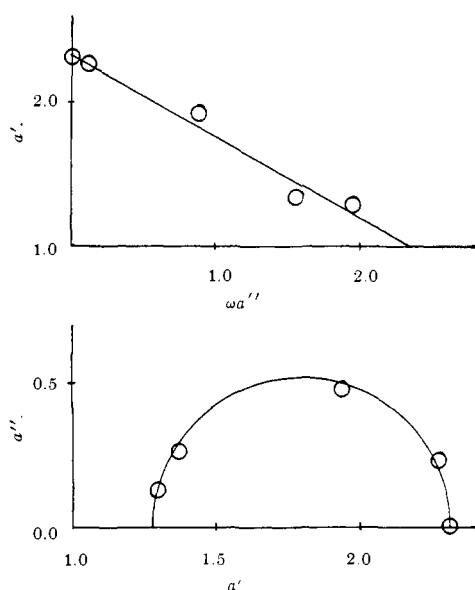


Fig. 1a (upper curve).—Plot of a' vs. $\omega a''$ for the triethylamine-trinitrobenzene complex in dioxane solutions at 35° .

Fig. 1b (lower curve).—Complex plane plot for triethylamine-trinitrobenzene complex in dioxane solution at 35° .

electric field

$$d[\text{DA}]/dt = -(k_1 + k_4)[\text{DA}] + k_2[\text{A}][\text{D}] + k_5[\text{AD}] \quad (4)$$

$$d[\text{AD}]/dt = -(k_1 + k_5)[\text{AD}] + k_2[\text{A}][\text{D}] + k_4[\text{DA}] \quad (5)$$

Subtraction of 5 from 4 gives

$$d\{[\text{DA}] - [\text{AD}]\}/dt = -(k_1 + 2k_4)[\text{DA}] + (k_1 + 2k_5)[\text{AD}] \quad (6)$$

which is zero for the equilibrium state.

$$[\text{AD}] = \{(k_1 + 2k_4)/(k_1 + 2k_5)\}[\text{DA}] \quad (7)$$

Since the electric field has no effect on the equilibrium between complex and constituents, $[\text{DA}] + [\text{AD}] = \text{constant} = N_p$. The dielectric polarization is proportional to the ratio

$$\frac{[\text{DA}] - [\text{AD}]}{[\text{DA}] + [\text{AD}]} = \frac{k_5 - k_4}{k_1 + k_4 + k_5} \quad (8)$$

At experimental field strengths, the exponential terms in μ and F may be expanded, giving

$$k_4 = k_3 \exp(-\mu F/kT) = k_3(1 - \mu F/kT) \quad (9)$$

$$k_5 = k_3 \exp(+\mu F/kT) = k_3(1 + \mu F/kT) \quad (10)$$

Using these equations, together with 8,

$$\frac{[\text{DA}] - [\text{AD}]}{[\text{DA}] + [\text{AD}]} = \frac{2(\mu F/kT)}{(k_1/k_3) + 2} \quad (11)$$

Equation 11 shows that if the rate of complex rupture, k_1 , is much greater (by a factor of ten or so) than the rate of relaxation, k_3 , the polar complexes can make no appreciable contribution to the total polarization of the system.

The dynamic case can be treated using eq. 6. If the field is suddenly removed at time $t = 0$ after equilibrium has been established, eq. 6 becomes

$$d\{[\text{DA}] - [\text{AD}]\}/dt = -(k_1 + 2k_3)\{[\text{DA}] - [\text{AD}]\} \quad (12)$$

since $k_3 = k_4 = k_5$ when $F = 0$. This differential equation has the solution

$$[\text{DA}] - [\text{AD}] = \{[\text{DA}] - [\text{AD}]\}_{t=0} \exp[-(k_1 + 2k_3)t] \quad (13)$$

Evaluating the boundary condition using 11, the result is

$$\{[\text{DA}] - [\text{AD}]\} = \frac{2(\mu F/kT)N_p}{(k_1/k_3) + 2} \exp[-(k_1 + 2k_3)t] \quad (14)$$

The experimental relaxation time is defined by the reciprocal of the coefficient in the exponential term of

14. The exchange mechanism coupled to orientational relaxation leads to

$$\tau = 1/(k_1 + 2k_3) \quad (15)$$

The common case of orientational relaxation alone gives $\tau = 1/(2k_3)$. Comparison of these two expressions shows that a rate of rupture of the same magnitude as that for orientation will indeed lower the experimental relaxation time.

If it is assumed that the polar molecular complex between iodine and benzene, or iodine and *p*-dioxane, should have a relaxation time of 10×10^{-12} sec. if it did not dissociate, a value of 5×10^{10} sec.⁻¹ is calculated for k_3 . This value, together with the experimental relaxation time of 3×10^{-12} sec., indicates a rate of rupture of about 2.3×10^{11} sec.⁻¹. From the equilibrium constants,⁶ rates of complex formation of 3.5×10^{11} sec.⁻¹ and 2.1×10^{12} sec.⁻¹ for the iodine-benzene and iodine-*p*-dioxane systems are obtained.

It has been observed that seemingly nonpolar solvents, e.g., benzene and carbon tetrachloride, exhibit losses in the frequency range above 24 kMc.¹⁵ Whiffen has proposed that these losses may be due to the orientation of short-lived moments arising because of molecular collisions. Under this hypothesis, molecular collisions occasionally cause a normally symmetric species to assume a polar, unsymmetrical configuration. This polar molecular configuration would then contribute to orientation polarization.

If the number of collision-induced molecular dipoles is independent of field strength under ordinary experimental conditions, these nonpolar systems can also be treated by the model discussed above. The dipolar molecular configuration may be aligned in either of two directions, and the symmetric configuration replaces the nonpolar constituent molecules of the charge-transfer case. The relaxation time of benzene molecules in the polar configuration may be estimated from the value measured for fluorobenzene in dilute carbon tetrachloride solution as 5×10^{-12} sec.¹⁶ Whiffen¹⁵ experimentally obtained a value of 1×10^{-12} sec. for benzene. From these values, eq. 15 gives an average lifetime of 1.3×10^{-12} sec. for benzene in a polar configuration.

Complexes of 1,3,5-Trinitrobenzene with Tertiary Amines.—The iodine-benzene and iodine-*p*-dioxane complexes represent relatively weak charge-transfer systems. On the other hand, the complex between 1,3,5-trinitrobenzene and a tertiary amine should be quite strong. Amines are a class of very powerful donors, and trinitrobenzene ranks with iodine and tetracyanoethylene in acceptor strength. Trinitrobenzene was used as the acceptor molecule in this study rather than iodine because the latter was found to interact with the silver-lined high frequency sample cells over a period of days. Tertiary amines were chosen as donors owing to their small dipole moments. These small moments facilitated interpretation of the experimental data. The use of the weak donor, *p*-dioxane, as a solvent was necessitated by the solubility of trinitrobenzene. The temperature of 35° was chosen for the same reason.

The trinitrobenzene-triethylamine system exhibited dielectric behavior which could be described in terms of a single relaxation time of 53×10^{-12} sec. The semicircular Cole-Cole arc in the complex plane is illustrated in Fig. 1b. Figure 1a shows the plot of a' vs. $\omega a''$ for the system. A relaxation time of 11×10^{-12} sec. was found for triethylamine under identical conditions. No loss could be observed for solutions of

(15) D. H. Whiffen, *Trans. Faraday Soc.*, **46**, 124 (1950).

(16) W. E. Vaughan, W. P. Purcell, and C. P. Smyth, *J. Am. Chem. Soc.*, **83**, 571 (1961).

trinitrobenzene alone within experimental accuracy. The single dispersion region found for the trinitrobenzene-triethylamine complex indicates that the triethylamine molecule is involved in a stable polar complex with trinitrobenzene.

No evidence of a molecular complex between trinitrobenzene and triphenylamine was observed. Just as the dielectric constant, ϵ , of a dilute solution of a polar solute in a nonpolar solvent may be expressed⁵ as

$$\epsilon = \epsilon_1 + a_1 N_1 \quad (16)$$

where ϵ_1 is the dielectric constant of the solvent, N_1 the mole fraction of solute i , and a_1 a constant characteristic of the total polarization of the solute molecule, the dielectric constant of a tertiary solution in which there is no interaction between solute molecules may be written

$$\epsilon = \epsilon_1 + a_1 N_1 + a_2 N_2 \quad (17)$$

For the 1:1 mole ratios of trinitrobenzene and tertiary amines used, this equation should represent the dielectric constants of dilute solutions if no complex is formed. As indicated in Table IV, the sum of the individual binary slopes agrees with that of the tertiary solution for the trinitrobenzene-triphenylamine system. The differences between the binary sum and the tertiary slope in the other two systems is an indication of a new polar species being formed. Further evidence for the lack of complexing between trinitrobenzene and triphenylamine is the agreement of the losses at 1.25 and 3.22 cm. for the tertiary solutions with those of triphenylamine itself.

TABLE IV
SLOPES OF THE STATIC DIELECTRIC CONSTANT IN *p*-DIOXANE
AT 35°

Solute	Solute + dioxane	C ₆ H ₅ (NO ₂) ₃ slope + amine slope	C ₆ H ₅ (NO ₂) ₃ + amine + dioxane
1,3,5-Trinitrobenzene	1.28
Triethylamine	0.34	1.62	2.32
Tributylamine	0.33	1.61	2.19
Triphenylamine	1.93	3.21	3.16

On the basis of electron spin resonance measurements, Turkevich and Stamires¹⁷ have concluded that the iodine-triphenylamine system exists largely as [(Ph)₃N...N(Ph)₃]⁺ and I₂⁻ radicals. Such radicals in the

(17) J. Turkevich and D. N. Stamires, *J. Am. Chem. Soc.*, **85**, 2557 (1963).

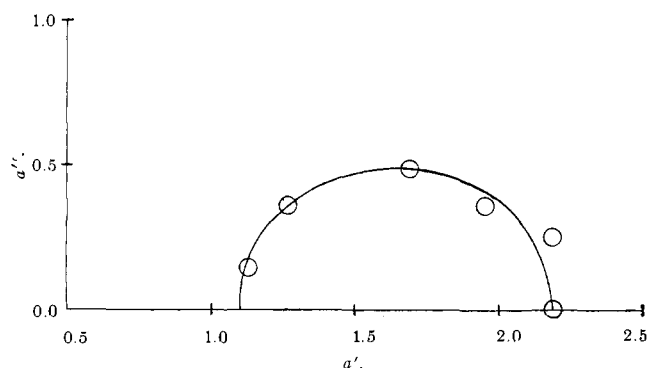


Fig. 2.—Calculated complex plane plot and experimental points for the tributylamine-trinitrobenzene system in dioxane at 35°.

trinitrobenzene-triphenylamine system would be consistent with the dielectric data, since neither of these radical species is dipolar. The observed additivity of the binary slopes would then be expected.

The trinitrobenzene-tributylamine system seems to be intermediate between the other two. The experimental data indicate a loss maximum at about 10 cm., but do not fit a Cole-Cole frequency distribution. A separation of the dispersion region in terms of two relaxation times was effected,¹⁸ using the experimental relaxation time 30×10^{-12} sec. of tributylamine as one parameter. A reasonable fit to the experimental data was obtained with $c_1 = c_2 = 0.5$, $a_\infty = 1.10$, and $\tau_c = 75 \times 10^{-12}$ sec.; τ_c is the apparent relaxation time of the trinitrobenzene-tributylamine complex, a_∞ is the infinite frequency intercept, and c_1 and c_2 are relative weighting parameters. The experimental points are shown in Fig. 2 together with the curve calculated from the above parameters. The separation in terms of two relaxation times indicates that there is a considerable amount of uncomplexed tributylamine in the system. In view of the spectroscopic data⁶ for the iodine complexes with triethylamine and tributylamine, this is not overly surprising. These latter measurements indicate that the iodine-tributylamine complex has an association constant about one-fourth that of the iodine-triethylamine. The greater bulk of the tributylamine molecule, which hinders close approach to an acceptor molecule, is probably responsible for this.

(18) K. Bergmann, D. M. Roberti, and C. P. Smyth, *J. Phys. Chem.*, **64**, 665 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

Isotope Effects in Recoil Tritium Reactions with Methyl Fluoride¹

BY EDWARD K. C. LEE AND F. S. ROWLAND

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The relative yields of radioactive products have been determined in mixtures of CH₃F and CD₃F with cyclobutane. The probability, per hydrogen atom in the target molecules, for forming CH₂TF from CH₃F is 0.61 ± 0.01 relative to the formation of cyclo-C₄H₇T + C₂H₅T from cyclobutane. The corresponding figure for CD₂TF from CD₃F is 0.46 ± 0.01 , indicating a probability integral isotope effect of 1.33 ± 0.04 for recoil tritium reactions with C-H bonds *vs.* C-D bonds. The yields of both CH₂TF from CH₃F and CD₂TF from CD₃F are independent of pressure within the accuracy of the measurements. A secondary isotope effect of 1.40 ± 0.05 is estimated for the replacement of F by T in CH₃F *vs.* CD₃F. The moderating ability of CH₃F and CD₃F for energetic tritium atoms is approximately equal. The isotope effect favoring replacement of H *vs.* D can arise from the formation of a short-lived transition complex, which breaks up by loss of H (or D) in competition with the T atom. The loss of the T atom corresponds to a highly inelastic "cushioning" collision.

Introduction

The energetics and mechanisms of reactions involving high energy tritium atoms have been the subject of a

(1) Research supported by A.E.C. Contract No. AT-(11)-407 and by fellowship support from the Pan American Petroleum Foundation (E. K. C. Lee).

number of recent investigations.²⁻¹¹ One of the most promising general areas of study involved in the study

(2) F. S. Rowland, J. K. Lee, B. Musgrave, and R. M. White, "Chemical Effects of Nuclear Transformations," International Atomic Energy Agency, Vienna, 1961, Vol. 2, p. 67.

(3) M. Henchman, D. Urch, and R. Wolfgang, *ibid.*, Vol. 2, p. 83.