rate constants are somewhat uncertain because of the previously described treatment of the data. An independent determination of the equilibrium constant would remove this uncertainty. However, the assumption of a diffusion-controlled association is consistent with the few available measurements of such rate constants.[6,7] The dissociation rate constant has a smaller value than found in pure dioxane, its activation energy is larger, and the over-all enthalpy change is more negative. All of these results are quite plausible and are consistent with the idea that the dissociation rate constant is a direct measure of the solvent competition for the hydrogen bonds of the solute.

In all of the solvent systems investigated, the standard enthalpy change is very small, less than $|-2.5|$ kcal/mole of hydrogen bonds. The entropy and volume changes parallel each other, as might be expected.

In summary, specific interactions, rather than macroscopic properties, are responsible for changes in hydrogen-bonding rates and equilibria observed in the various solvents, and kinetic studies provide a tool for probing microscopic solvent structure. In all cases hydrogen-bond formation and dissociation is a rapid process, and hydrogen-bond exchange times are certainly fast enough to permit the most rapid known transformations of polypeptides[13,20] and proteins.[8] Future work will be concerned with investigations of other types of hydrogen bonds.

Acknowledgment. H. O. S. is grateful to Dr. Thomas B. Lewis for helpful instruction on the ultrasonic technique.

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Hydrogen Isotope Effects in the Vapor-Phase Radiolysis of Water

John Y. Yang and Inge Marcus

Contribution from the North American Aviation Science Center,
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Abstract: Tritium-labeled water and 1:1 H_2O–D_2O solutions, each containing cyclopentane as additive, were irradiated in the vapor phase by Co^{60} γ rays. Isotopic analyses of the radiolytic hydrogen led to the calculated values of $\alpha_T = 1.7 \pm 0.1$ and $\alpha_D = 1.2 \pm 0.1$ as the relative rates for H *vs.* T and H *vs.* D atom formations. These values are much smaller than the values of 2–6 reported for the deuterium isotope effect in the radiolysis of liquid water, indicating that different reaction processes are involved.

Although differences in zero-point energies between hydrogen isotopes (protium, deuterium, and tritium) seem negligibly small relative to the high energies available in radiation-induced reactions, significant isotope effects are often observed. The values reported for "molecular" hydrogen and hydrogen-atom formations,[1-3] as well as those observed for hydrogen abstraction by hydrogen atom and other radical intermediates,[4,5] are surprisingly large.

In the radiolysis of water and dilute aqueous solutions, where the reaction processes are reasonably well established,[6] numerous estimates of isotope effects for both "molecular" hydrogen and hydrogen-atom formations have been made.[1-3] There estimated values are highly sensitive to possible effects of added solutes on the rather complex series of reaction processes. Isotope effects are found to be somewhat different in acid and neutral solutions, and the hydrogen relative to deuterium-enrichment values (α_D) for both "molecular" hydrogen and hydrogen-atom formations varied between 2 and 6.

Recent investigations[7-10] have demonstrated that in the radiolysis of water vapor, a relatively simple set of reaction processes is involved. In the absence of tracer impurities, back reactions of hydrogen atoms and hydroxyl radicals take place effectively, and very little products are observed. In the presence of organic additives, these intermediates undergo hydrogen-abstraction reactions to give large yields of hydrogen. From a study of the hydrogen isotopic composition relative to that in the reactant water, we have calculated isotope effects for the hydrogen-atom formation.

Experimental Section

Materials. Cyclopentane and cyclohexane were Phillips research grade products, and were further purified by slow passage through 2-ft silica gel columns to remove unsaturated hydrocarbon contaminants. Phillips research grade ethylene was purchased from the Matheson Co., and it was used without purification except for the usual degassing at 77°K. Deuterium oxide was purchased from the Oak Ridge National Laboratory and tritium-labeled water from the New England Nuclear Corp. Both the deuterated and the tritiated water samples were treated by Co^{60} γ irradiation, followed by degassing and photolysis with long-wavelength ultraviolet light.[11] Ordinary water was purified by the usual procedure

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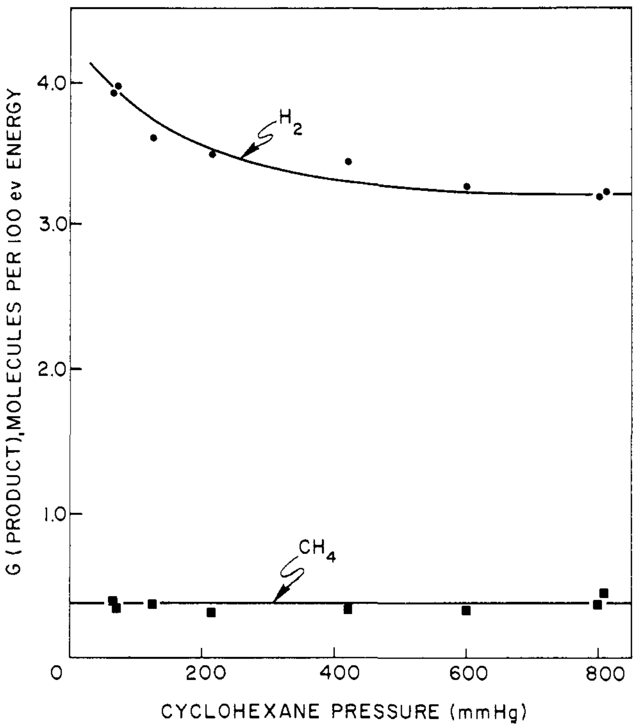

Figure 1. Methane and hydrogen yields from vapor-phase radiolysis of cyclohexane.

of distillation through alkaline permanganate and acid dichromate solutions. Mass spectrometric analyses showed that our D_2O sample was 99% isotopically pure. The D_2O-H_2O mixture was made up to give a D:H ratio of 1:1. Its composition was verified by mass spectrometric analyses of samples of the mixture after these had been converted to hydrogen gas by heating at 500° for 3 hr in Pyrex 1720 ampoules in the presence of zinc dust.

Irradiations. Cylindrical sample cells, about 250-ml volume and equipped with breakoff seals, were baked at 400° for a minimum of 24 hr while being evacuated to a pressure of less than 1×10^{-6} mm. Water and hydrocarbon samples were degassed and sealed into small ampoules. Individual samples were weighed, opened under vacuum, and further degassed before being distilled into the irradiation cells. Irradiations were carried out in a modified Atomic Energy of Canada Gamma-Cell, Model 200 (10,000 curies), Co^{60} γ source. Samples were heated to 120–135° and irradiated to the desired doses at these temperatures. The total pressure for each sample was about 800 mm unless otherwise specified.

Dosimetry. The Co^{60} γ-dose rate was determined by the radiolysis of ethylene at the ambient source temperature of 40° and gas pressure about 700 mm. The total yield of noncondensable gas at 77°K was determined by volume–pressure measurements, and the hydrogen and methane contents were obtained by mass spectrometric analysis. Taking the value of $G(H_2) = 1.3$ for ethylene radiolysis,[12–14] our dose rate was calculated as 1.1×10^{20} ev/hr/g of C_2H_4. The dose absorption in the water-vapor mixtures was estimated by the usual technique of adjusting for differences in the electron densities for individual samples. Such dose measurements may be in error by about 10%. However, since only relative yields are involved in our study, any error in the dose rate measurements will not affect our isotope-effect calculations.

Analysis. The product gas noncondensable at 77°K was measured, collected, and analyzed by mass spectrometry. In irradiations of water–hydrocarbon mixtures, hydrogen gas was always found in excess of 99% of the total noncondensable gas. The total hydrogen yield as well as the isotopic hydrogen composition of the product gas from deuterium-containing samples were thus determined. The specific activity of the tritium-labeled water was analyzed by liquid scintillation counting using a Packard Tri-Carb Model 314EX instrument, and that of the radiolytic hydrogen by ion-chamber measurements using a Cary Model 31 vibrating reed electrometer. The relative sensitivities for liquid scintillation counting and ion-chamber measurements were calibrated by converting tritiated water samples to hydrogen gas by the zinc-reduction procedure. Complete conversion was ascertained by weighing the water sample and measuring the product hydrogen gas.

Results

A complete understanding of the reaction mechanism for water-vapor radiolysis is still lacking. It has been shown by Baxendale and Gilbert[8] that the observed yields of radical intermediates are consistent with the following sequence of reactions.

$$H_2O \rightsquigarrow H_2O^+ + e \tag{1}$$

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH \tag{2}$$

$$H_3O^+ + e \longrightarrow H + H_2O \tag{3}$$

On the other hand, the over-all reaction processes leading to hydrogen formation in the vapor-phase radiolysis of water–hydrocarbon mixtures are well established,[8,9] and these may be represented as

$$H_2O \rightsquigarrow H,\ OH,\ H_2,\ \text{etc.} \tag{4}$$

$$RH \rightsquigarrow H_2 + \text{other products} \tag{5}$$

$$H + RH \longrightarrow H_2 + R \tag{6}$$

The detailed mechanisms are not specified, and, furthermore, the origin of the "molecular" hydrogen yield in reaction 4 is not known. Even the possible formation by hydrogen-atom combination cannot be ruled out. In this study we shall attempt only to interpret our results on the basis of known over-all processes.

For mixtures with about 5% organic additives in water, the bulk of the radiolytic hydrogen arises by reaction 6. In the presence of D_2O, the isotope effect for hydrogen-atom *vs.* deuterium-atom production may be measured from the observed H_2/HD ratio, correcting for small direct hydrogen yields from reactions 4 and 5. Direct hydrogen formation by reaction 5 will give only H_2, and we shall denote the H_2 yield from this source as $(H_2)_a$. "Molecular" hydrogen yields by reaction 4 in a H_2O–D_2O mixture will consist of H_2, HD, and D_2, and these yields shall be denoted as $(H_2)_m$, $(HD)_m$, and $(D_2)_m$, respectively. We can express the isotope effect α_D (the enrichment of the H/D ratio in the product relative to that in the reactant) as

$$\alpha_D = \frac{(H_2) - (H_2)_a - (H_2)_m}{(HD) - (HD)_m} \tag{7}$$

where (H_2) and (HD) represent the observed H_2 and HD yields. The H_2 yield by reaction 5 can be easily estimated from a study of the vapor-phase radiolysis of the pertinent hydrocarbon. Contributions of $(H_2)_m$ and $(HD)_m$ obviously depend both on the magnitude of such "molecular" hydrogen yields and on a possible isotope effect in the direct hydrogen formation by reaction 4. Since $(H_2)_a$, $(H_2)_m$, and $(HD)_m$ are relatively small correction terms, any reasonable deviations in our estimate of these values should result only in small errors in the calculated isotope effect values.

Vapor-Phase Radiolysis of Cyclohexane and Cyclopentane. The hydrogen and methane yields from the radiolysis of cyclohexane vapor at 120° have been determined as functions of the sample pressure, and the results are presented in Figure 1. The methane yield

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appears to be pressure independent within the range of 70–800 mm with $G(CH_4) = 0.40$. The hydrogen yield is essentially constant at relatively high cyclohexane pressures with $G(H_2) = 3.5$, but at the pressure about 70 mm $G(H_2) = 4.0$. Irradiations of two cyclopentane samples at 70 mm similarly gave $G(H_2) = 4.0$. These values are much smaller than the values of $G(H_2) = 5.3$, $G(CH_4) = 0.5$ and $G(H_2) = 4.8$, $G(CH_4) = 0.36$ reported respectively by Blachford and Dyne[15] and Theard[16] for similar irradiations. We wish to point out, however, that the literature values were calculated as the initial H_2 and CH_4 yields, whereas our observed yields correspond only to irradiations with a total dose of 3.5×10^{20} ev/g of sample.

The ionization potential of water (12.6 ev) is much higher than that of cyclopentane (10.5 ev), and one might expect charge or energy transfer to occur, resulting in higher hydrogen yields from cyclopentane in the presence of water. In order to test for this possibility, we have irradiated D_2O–C_5H_{10} mixtures. The hydrogen-yield data are given in Table I, and the $G(H_2)$ values, based on energy partition proportional to the electron fraction, are calculated and given in the last column. The H_2 yield must result from reactions involving only cyclopentane, and the average value of $G(H_2)$ is identical with that observed in the absence of water vapor. We conclude therefore that energy transfer between water and cyclopentane does not take place. Since water molecules are easily protonated, our observation is thus in agreement with the proposal of Toma and Hamill[17] for liquid-phase radiolysis that protonation tends to take precedence over charge exchange. Therefore, we shall assume that the yield of H_2 due to reaction 5 is given by

$$(H_2)_a = \frac{4.0\epsilon}{G(\text{hydrogen})} \times 100 \qquad (8)$$

where ϵ is the electron fraction of cyclopentane and $(H_2)_a$ is given as the per cent of the total hydrogen yield.

Table I. Hydrogen Yields from Irradiations of D_2O–C_5H_{10} Mixtures[a]

ϵ[b]	G (hydrogen)	—Isotopic compn, %— H_2	HD	D_2	$\%H_2 \times G$ (hydrogen)/ $\epsilon \times 10^2$
0.035	5.6	2.5	91.0	6.5	4.0[c]
0.057	5.8	4.1	89.9	6.0	4.1
0.111	6.2	7.1	86.6	6.3	4.0

[a] Total dose = 3.5×10^{20} ev/g of sample. [b] Electron fraction of C_5H_{10}. [c] Values in this column correspond to the $G(H_2)$ yields resulting from direct energy absorption in cyclopentane.

"Molecular" Hydrogen Yield in the Radiolysis of Water Vapor.[18] Firestone[7] showed that, in the radiolysis of pure water vapor in thoroughly degassed cells, $G(H_2)$ is less than 0.02. However, it has been suggested by Baxendale and Gilbert[9] that in the presence of organic additives "molecular" hydrogen yields with $G = 0.5$ are formed. In the irradiations of D_2O–H_2 and D_2O–C_3H_8 mixtures,[9] they reported $G(D_2) = 0.5$. Similarly in our irradiations of D_2O–C_5H_{10} mixtures, we have calculated from data in Table I values of $G(D_2) = 0.4$. In several irradiated D_2O and C_5H_8 (cyclopentene) samples we also found $G(\text{hydrogen}) = 1.2$ and $G(D_2) = 0.4$. Our hydrogen-yield data in the radiolysis of H_2O–D_2O–C_5H_{10} mixtures are given in Table II. As we shall demonstrate later, the $(H_2)_m$, $(HD)_m$, and $(D_2)_m$ yields can be calculated, and the average G value for "molecular" hydrogen yields is shown again to be about 0.5.

Table II. Hydrogen Yields in the Radiolysis of H_2O–D_2O–C_5H_{10} Mixtures[a]

ϵ[b]	G (hydrogen)	—Isotopic compn, %— H_2	HD	D_2	α_D[c]	G(m)[d]
0.021	5.0	50.9	46.7	2.4	1.10	0.48
0.032	5.0	50.7	46.8	2.5	1.09	0.49
0.053	5.4	56.0	41.9	2.1	1.33	0.56
0.087	5.8	53.9	43.9	2.2	1.16	0.54
0.095	5.7	53.9	43.8	2.3	1.14	0.55

[a] Total dose = 3.5×10^{20} ev/g of sample. [b] Electron fraction of C_5H_{10}. [c] Calculated isotope effect for H-atom *vs.* D-atom formation. [d] Calculated "molecular" hydrogen yield.

In the radiolysis of 1:1 H_2O–D_2O samples, the H/D ratio in the resulting "molecular" hydrogen is given as

$$\frac{2(H_2)_m + (HD)_m}{2(D_2)_m + (HD)_m} = \alpha_D \qquad (9)$$

For simplicity, we assume isotope effects for hydrogen formation by molecular and atomic processes to be about the same. Assuming either the "molecular" yield arises by hydrogen-atom recombination or by molecular detachment in which the isotope effect for H_2/HD formation is about the same as that for HD/D_2 formation, we expect, by statistical considerations

$$\frac{(HD)_m{}^2}{(H_2)_m(D_2)_m} = 4 \qquad (10)$$

Solution of eq 9 and 10 gives

$$(H_2)_m = \alpha_D{}^2(D_2) \qquad (11)$$

and

$$(HD)_m = 2\alpha_D(D_2) \qquad (12)$$

where (D_2), the observed yield, is identical with $(D_2)_m$ since the additive hydrocarbon does not contain deuterium. Thus, $(H_2)_m$ and $(HD)_m$ yields can be evaluated from the D_2 content of the radiolytic hydrogen. The total "molecular" hydrogen yields from the radiolysis of 1:1 H_2O–D_2O solutions are given as G(m) in Table II. The average value of $G(m) = 0.52$ is in good agreement with "molecular" hydrogen yields reported for a variety of water vapor–organic additive mixtures. We feel therefore that the approximations made for eq 9 and 10 are reasonable.

H-Atom *vs.* D-Atom Formation. We have irradiated 1:1 H_2O–D_2O mixtures containing cyclopentane, and the isotopic hydrogen yield data are summarized in Table II. The hydrogen-atom isotope effect, α_D, is

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[15] J. Blachford and P. J. Dyne, *Can. J. Chem.*, **42**, 1165 (1964).

[16] L. M. Theard, *J. Phys. Chem.*, **69**, 3292 (1965).

[17] S. Z. Toma and W. H. Hamill, *J. Am. Chem. Soc.*, **86**, 4761 (1964).

[18] The term, "molecular" hydrogen, is used here to denote hydrogen formation from water molecules alone by any processes other than by hydrogen-atom intermediates. The reaction mechanism is not known, and both unimolecular and bimolecular processes are possible.

calculated by

$$\alpha_D = \frac{(HD) \pm \{(HD)^2 - 4(D_2)[(H_2) - 4.0\epsilon/G(\text{hydrogen})]\}^{1/2}}{2(D_2)} \quad (13)$$

which is obtained from eq 7 by appropriate substitutions for $(H_2)_a$, $(H_2)_m$, and $(HD)_m$. The calculated α_D values are listed in Tables II, giving an average value of 1.16 for the isotope effect in favor of H-atom over D-atom formation.

H-Atom *vs.* T-Atom Formation. The G value for hydrogen-atom formation in the vapor-phase radiolysis of water (H_2O or D_2O) has been estimated[7-9] to be about 8–11. In our irradiations of H_2O–D_2O–C_5H_{10} mixtures, the G(hydrogen) yields are only about 5. Thus, only about 50% of the hydrogen atoms from dissociation of water molecules abstract hydrogen from cyclopentane. This leads to a reasonable doubt as to whether our calculated deuterium isotope effect truly represents the relative rate of H-atom *vs.* D-atom formation. In order to confirm our calculations for α_D, it seems logical to measure analogous tritium-atom isotope-effect (α_T) values.

Since tritium analysis is very sensitive, it is possible to make measurements at very low total hydrogen yields. Thus, we were able to irradiate tritiated water–cyclopentane mixtures to very low conversions, giving rise to higher G(hydrogen) yields. With large variations in both the cyclopentane content and the total dose absorption, the G(hydrogen) values varied between 3.4 and 6.9. The isotopic hydrogen yield data from these experiments are given in Table III and presented in the order of decreasing total hydrogen yields. We assume again that the "molecular" hydrogen results from hydrogen-atom recombination with $G(\text{m}) = 0.5$, and that hydrogen is formed from direct energy absorption in cyclopentane with $G(H_2) = 4.0$. The specific tritium activity in the resulting radiolytic hydrogen, A_{gas}, is then given as

$$A_{\text{gas}} = \frac{0.5A_{\text{water}}/\alpha_T + {}^1/_2[G(\text{hydrogen}) - 0.5 - 4.0\epsilon]A_{\text{water}}/\alpha_T}{G(\text{hydrogen})} \quad (14)$$

where A_{water} is the tritium specific activity of the reactant water and α_T represents the relative enrichment of H-atom *vs.* T-atom formation. Equation 14 is rearranged to give

$$\alpha_T = \frac{{}^1/_2[G(\text{hydrogen}) - 4.0\epsilon + 0.5]}{(A_{\text{gas}}/A_{\text{water}})G(\text{hydrogen})} \quad (15)$$

The calculated α_T values are listed in Table III, giving an average value for the isotope effect of 1.68.

The above α_T value remained constant within a twofold change in the total hydrogen yield. It appears that the combined effects of other competing processes, such as the back reaction of hydrogen atom and hydroxyl radical recombination, do not exhibit an appreciable isotope effect. Therefore, we may conclude that our calculated α_D and α_T values truly represent the relative rates for H-atom *vs.* D-atom and H-atom *vs.* T-atom formations in the vapor-phase radiolysis of water.

Table III. Hydrogen Yields in the Radiolysis of Tritiated Water–Cyclopentane Mixtures[a]

ϵ[b]	Total dose, ev/g × 10^{-20}	G(hydrogen)	$A_{\text{gas}}/A_{\text{water}}$[c]	α_T[d]
0.101	0.1	6.9	0.308	1.65
0.056	0.2	6.0	0.320	1.64
0.045	0.6	5.5	0.301	1.77
0.056	2.4	5.0	0.293	1.80
0.154	12.0	4.7	0.294	1.66
0.122	12.0	4.5	0.312	1.61
0.042	12.0	4.1	0.327	1.67
0.033	12.0	3.5	0.329	1.70
0.008	12.0	3.4	0.343	1.68

[a] Specific activity of water = 16.2 μcuries/mg of H). [b] Electron fraction of C_5H_{10}. [c] A_{gas} and A_{water} represent the tritium specific activity in the radiolytic hydrogen and that in the reactant water sample, respectively. [d] Calculated isotope effect for H-atom *vs.* T-atom formation.

Discussion

The isotope-effect value of α_D, which we have obtained for vapor-phase radiolysis, is much smaller than corresponding values of 2–6 reported in the radiolysis of liquid water.[1-3] It is known that the deuterium isotope effects in acid and in neutral aqueous solutions are much different, and so Anbar and Meyerstein[3,4] proposed that at least two different processes such as reactions 16 and 17 are responsible for hydrogen-atom formation in the liquid phase. In acid solutions, reaction 17 becomes more important and a significantly larger deuterium isotope effect is observed. However, even in neutral aqueous solutions, α_D is found greater than 2. It is not unlikely that the hydrogen-atom formation in the vapor phase takes place by a reaction different from either of the two processes occurring in the liquid phase.

$$H_2O^* \longrightarrow H + OH \quad (16)$$

$$e_{eq}^- + H_3O^+ \longrightarrow H + H_2O \quad (17)$$

Fiquet-Fayard[19] has shown by statistical arguments that, at deuterium contents near 100%, a deuterium isotope effect greater than 2 must indicate that more than one water molecule is involved in the reaction producing hydrogen atoms. Certainly, reaction 16 need not be as simple as it is represented. In the condensed medium, where collision with another water molecule will easily take place, the mode of H_2O^* dissociation may be very complex.

Our observed isotope effect for the vapor-phase hydrogen-atom formation may be considered briefly on the basis of the sequence of reactions 1, 2, and 3 as possible primary processes for the decomposition of the water molecule. By analogy to facile proton exchange between water molecules, little potential-energy barrier

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(19) F. Fiquet-Fayard, *J. Chim. Phys.*, **57**, 467 (1960).

and isotope effect are expected for reaction 2. Reaction 3, however, may proceed through an excited intermediate as represented by

$$H_3O^+ + e \longrightarrow H_3O^* \longrightarrow H + H_2O \qquad (18)$$

Our observed low value for the isotope effect in the gas phase may imply simply that thermal equilibration of excited intermediates is less likely than that in the liquid medium.

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Dipole Moments of Amine–Iodine "Complexes." A Question[1]

K. Toyoda[2] and Willis B. Person

Contribution from the Department of Chemistry, University of Iowa,
Iowa City, Iowa. Received November 4, 1965

Abstract: Experimental measurements of the dipole moments of three amine–iodine "complexes" confirm the values previously reported for the pyridine–iodine complex (Kortum and Walz) and also for the triethylamine–iodine complex (Tsubomura and Nagakura). An analysis of the atomic and electronic polarization terms establishes that the order of magnitude of the error introduced when these terms are neglected in the usual treatment of data from complexes is about 10%, for either weak or strong complexes with I_2. The very large values for the experimental dipole moments of the trialkylamine–iodine complexes in dioxane solution, combined with the ultraviolet spectra, suggest very strongly that the predominant species in these solutions is an ion pair with I_3^- as the negative ion. Thus, the very important values of the dipole moments of these complexes remain in question.

From the theoretical point of view, one of the more interesting experimental properties of electron donor–acceptor complexes is the dipole moment. As Mulliken[3] noted, the dipole moment of the complex can be directly related to the coefficient, b, measuring the contribution of the dative structure to the structure of the complex

$$\psi_N = a\psi_0 + b\psi_1 \qquad (1)$$

Here ψ_N is the wave function for the complex in its ground state. Its approximate form is given in terms of two hypothetical idealized structures, the "no-bond" state (D...A) with wave function ψ_0, and the "dative" state ($D^+–A^-$), with wave function ψ_1. The coefficients a and b measure the importance of each of these hypothetical states.

According to Mulliken,[3] for a weak complex between nonpolar molecules, the dipole moment of the complex is given approximately by

$$\mu \simeq b^2\mu_1 \qquad (2)$$

The value of μ_1, the dipole moment of the dative structure, can be estimated from a knowledge of the geometry of the complex; in general, it will be quite large because of the high charge separation in the dative structure. Hence, a measurement of the dipole moment of the complex can give a direct measure of the coefficient b. The application of these ideas has been illustrated by Briegleb[4] for some complexes.

A careful examination of the dipole moment data reviewed by Briegleb[4] reveals that agreement on the experimental values found by different workers is not always perfect. Further consideration suggests that one should observe caution in this interpretation of the data, since one must remember that the electronic and atomic polarization of the complex might change significantly from that of the components, thus leading to an apparent dipole. This subject has been discussed by Anderson and Smyth,[5] who have illustrated the power of the technique of measuring dielectric constants over a wide range of frequencies as applied to these complexes. They have shown that the benzene–iodine and dioxane–iodine complexes dissociate at a rate comparable to the rate of relaxation of the polar complex in solution, thus complicating the results.

In our studies we were concerned with some relatively strong amine complexes of I_2 with the goal of obtaining b values so that these may be used to correlate with other properties of these complexes, particularly the infrared spectrum.[6] Because of the known lack of reproducibility in the literature of dipole moments of complexes, and because of the general reactivity of I_2 with amines and with metal cells, etc., it seemed desirable to repeat measurements already given for pyridine–iodine[7,8] and for triethylamine–iodine.[9] Since the most complete far-infrared study on I_2 complexes is that by Yada, Tanaka, and Nagakura[10] on the tri-

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(2) On leave of absence from Department of Chemistry, Kumamoto University, Kumamoto, Japan, 1963–1964. Reprint requests should be directed to Dr. Person.

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