and the high ionic strength may make it even more positive.

Steric hindrance to solvation of the transition state would not be expected to lead to the rate facilitation seen with 3,3-dimethylbutyryl phosphate. Therefore, if there is smaller hydration change upon going from ground state to transition state with the 3,3-dimethylbutyryl acyl group it must be because of increased ground-state hydration as is also probable in the case of N-3,3-dimethylbutyryl imidazolium ion.[3] The rates of acid-catalyzed hydrolysis measured in 25% dioxane–water are consistent with solvent ordering in the ground state for 3,3-dimethylbutyryl phosphate since its rate was decreased much more than that of the two other compounds studied. This could be due to preferential solvation of the highly branched acyl group by the dioxane component of the solvent.

It would thus appear that the values of k_H for the acyl phosphates, which show a smaller sensitivity to steric bulk in the acyl group and a faster rate for 3,3-dimethylbutyryl phosphate than expected for an A2 reaction, and the unusual differences brought about by increasing acid concentrations can be explained either by increasing unimolecular character in the rate-determining step as branching in the acyl group increases, or smaller differences in hydration between ground state and transition state with greater acyl group branching, possibly due to the ability of alkyl groups to structure water around them in the ground state. These effects are not mutually exclusive and it is possible that both types of effects are important.

Acknowledgment. This work was supported by research grants from the National Institutes of Health and the American Cancer Society. Support for David R. Phillips was provided by National Institutes of Health Research Training Grant GM 197. We also acknowledge the assistance of Lily H. Brod in synthesizing the substituted benzoyl phosphates.

Ethyl Vinyl Ether Hydrolysis in Dimethyl Sulfoxide as Solvent[1a]

Maurice M. Kreevoy and Joel M. Williams, Jr.[1b]

Contribution from the School of Chemistry of the University of Minnesota, Minneapolis, Minnesota 55455. *Received May 24, 1968*

Abstract: When water, strong acid, and ethyl vinyl ether are all solutes in DMSO the rate of hydrolysis of the vinyl ether is still controlled by the rate of proton transfer to carbon. This rate is dissected, giving rate constants for the DMSO-solvated proton, k_H, and the monohydrated proton, k_{H_3O}, the former being about twice as large as the latter. This shows that direct proton transfer from strong acid to a carbon atom is possible, without an intervening water molecule and other evidence suggests that this is the predominant mechanism even when water is the solvent. If isotope effects on k_{H_3O} are assumed to be the same as those in water, reasonable and internally consistent isotope effects on k_H can be estimated. The variation in rate as a function of solvent composition is analogous to that for A1 reactions, and quite different from that for A2 reactions.

In a number of previous papers[2–4] detailed studies of proton transfers from aqueous acid to organic substrates have been reported. In none of these has it been possible to prove, definitively, the value of n in Figure 1. No evidence requiring that it be greater than zero has been developed, but, similarly, no evidence requiring that it be identically zero has been produced. In a recent paper[5] Goodall and Long have inferred that $n = 0$ for protonation of nitroalkane anions. Their inference, however, depends on assumptions about the transition state which, although reasonable, lack experimental support. It does not seem likely that definitive evidence on this point will be forthcoming for aqueous solutions.

The present paper reports results obtained in dilute solution in dimethyl sulfoxide (DMSO) with water present as a solute. The reaction chosen for study was ethyl vinyl ether cleavage (eq 1) which has already been

$$\mathrm{CH_2{=}CHOEt + H_2O \longrightarrow CH_3CH{=}O + EtOH} \tag{1}$$

extensively studied in aqueous solution. The results rigorously demonstrate that n equals zero in at least one case. While they apply directly only to the system actually studied, certain features of the results strongly suggest that the conclusions apply to aqueous solutions as well.

Results

Equilibrium Constants. If water is added to DMSO containing a small concentration of dissociated acid a series of hydrates, $H^+(H_2O)_m$, should be formed. In the limit, at very low water concentration, the equilibrium for the formation of the first of these (eq 2) can

$$\mathrm{H^+ + H_2O \overset{K_H}{\rightleftharpoons} H\cdot H_2O^+} \tag{2}$$

be studied. (All the species in eq 2 are DMSO solvated.) In the presence of an acid–base indicator

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[1] (a) Supported, in part, by the National Science Foundation through GP-7915. (b) National Science Foundation Postdoctoral Fellow, 1966–1967.

[2] M. M. Kreevoy and R. Eliason, *J. Phys. Chem.*, 72, 1313 (1968). This paper gives numerous references to earlier work on ethyl vinyl ether cleavage.

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[4] M. M. Kreevoy, P. J. Steinwand, and W. V. Kayser, *J. Am. Chem. Soc.*, **88**, 124 (1966).

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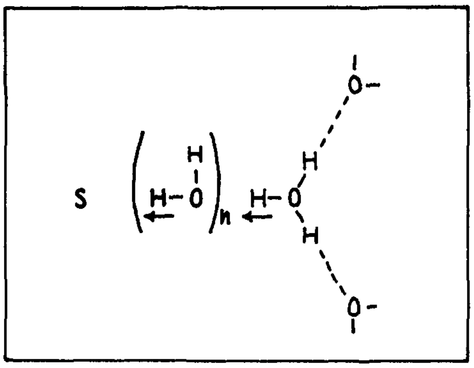

Figure 1. A generalized scheme for the transfer of a proton from an aqueous acid to an organic substrate; *n* may be zero or some small integer.

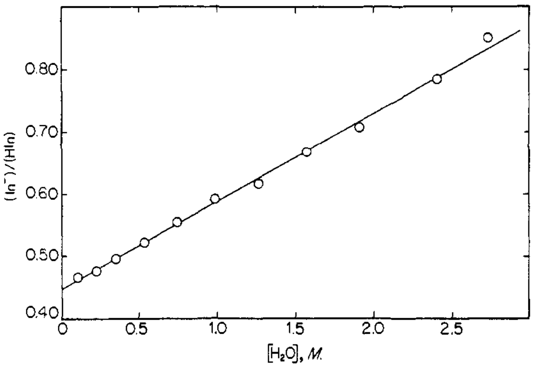

Figure 2. The effect of D_2O on the ratio of unprotonated to protonated indicator in a solution containing 3.2×10^{-5} *M* 2,6-dinitro-4-chlorophenol and 4×10^{-4} *M* DCl in anhydrous DMSO.

(2,6-dinitro-4-chlorophenol) the water competes with the basic form of the indicator for H^+, leading to eq 3.[6]

$$\frac{(\text{In}^-)}{(\text{HIn})} = \frac{K_I}{C_a}\{K_H(H_2O) + 1\} \qquad (3)$$

The ratio of unprotonated to protonated (neutral) form of the indicator can be determined spectrophotometrically. A plot of that ratio against water concentration should yield a straight line with K_I/C_a (the indicator dissociation constant over the stoichiometric strong acid concentration) as the intercept and $K_I K_H/C_a$ as the slope. Kolthoff and Reddy[6] have shown such a plot to be linear, and obtained 0.46 for K_H by dividing the latter by the former. This work has now been repeated with $\sim 10^{-4}$ *M* HCl at 25°. Equation 3 accurately describes $(\text{In}^-)/(\text{HIn})$ up to ~ 1.5 *M* H_2O and a value of 0.39 was twice obtained for K_H. Entirely similar experiments were carried out in D_2O. The results shown in Figure 2 yield a value of 0.32 for K_D. The 50% confidence limits (probable errors) for the slopes of these plots is 1.5%, and those on the intercepts, 0.5%, so that the statistical uncertainty in K_H or K_D is 2%. A more realistic value of the likely uncertainty in K_H or K_D is probably 20%, the difference between the present value of K_H and that of Kolthoff and Reddy. However, since most systematic errors would cancel in taking K_H/K_D, the ratio, 1.2, probably has not much more than its statistical uncertainty, 4%.

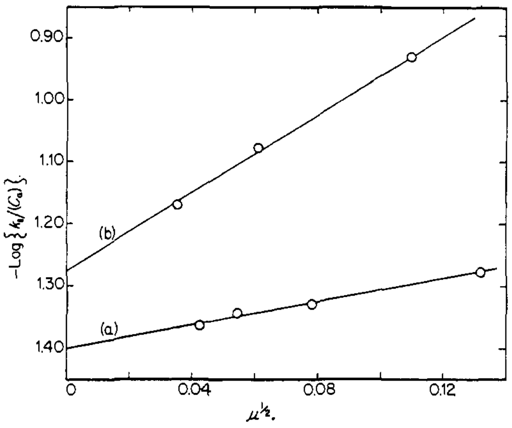

Figure 3. Variation of log (k_1/C_a) with $\mu^{1/2}$: a, 90 vol % (69.8 mol %) DMSO; b, 98 vol % (92.5 mol %). The best extrapolation to infinite dilution is shown.

Rate Constants. The rates were measured spectrophotometrically by monitoring the buildup of the acetaldehyde absorption at 286 mμ in various mixtures of DMSO, H_2O, and HCl (or, in certain cases, D_2O and DCl) at 25°. The formal HCl concentrations were always below 0.2 *M*. The vinyl ether was added as 10–50-μl samples. In all cases the integrated form of the first-order rate law, eq 4,[7] was obeyed to at least

$$k_1 = \frac{2.303}{t - t_0}\log\frac{D_\infty - D_0}{D_\infty - D_t} \qquad (4)$$

95% completion. (The symbols have their usual significance.) The pseudo-first-order rate constants, k_1, were evaluated graphically, and could be replicated with discrepancies of not more than 2–3%.

When the water content was 58 vol % and above, the quantity, k_1/C_a, at any given water content was invariant under changes in formal HCl concentration. At each such water concentration second-order rate constants, k_2, were obtained by averaging two or three values of k_1/C_a. At lower water concentrations k_1/C_a showed a systematic trend toward lower values at lower C_a. At each such water concentration log (k_1/C_a) was found to be a linear function of $\mu^{1/2}$ for μ (ionic strength) less than 0.01. At higher μ the variation in log (k_1/C_a) with $\mu^{1/2}$ became less pronounced. Typical plots of log (k_1/C_a) against $\mu^{1/2}$ are shown in Figure 3. For these water concentrations k_2 was obtained visually from the intercepts of such plots. Table I gives the values of k_2 and, where appropriate, *B*, the coefficient of $\mu^{1/2}$ required to correlate log (k_1/C_a).

Similar measurements were made in DMSO–D_2O (95:5) containing small concentrations of DCl. These gave a typical plot of log (k_1/C_a) against $\mu^{1/2}$, leading to values of 1.86×10^{-2} M^{-1} sec^{-1} for k_2^{D}[8] and 2.3 for k_2^{H}/k_2^{D}.[8]

When k_2 was obtained by simply averaging, in solutions containing at least 42% water, the usual spread of the extremes was about 5%. The estimated uncertainty in the values obtained by extrapolation is about the same. The uncertainty in k_2^{H}/k_2^{D} is, then, about 10%.

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[7] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York, N. Y., 1961, p 38.

[8] Where k_2^{H} is being contrasted with k_2^{D}, the isotope is designated by a superscript. In other places the superscript is omitted and the isotope is always H.

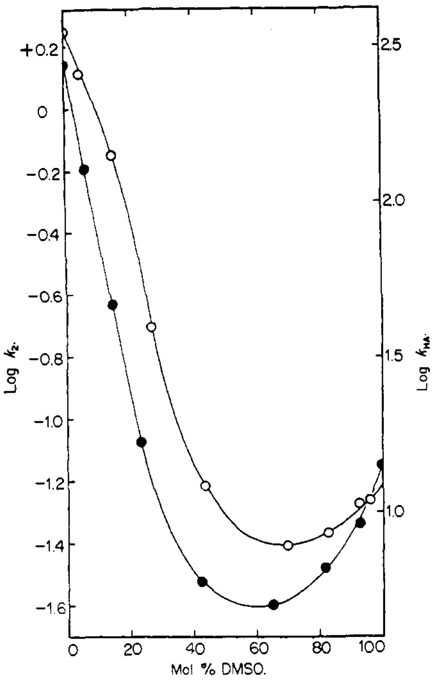

Figure 4. Rate and indicator acidity. Open points are rate data taken from Table I. Closed points refer to ratios of protonated to nonprotonated *p*-nitroaniline (HA) at infinite dilution.[9]

Isotope Effect by Competition. Using the general techniques of Kreevoy and Eliason[2] the reaction was carried out in solutions containing 5 vol % (17.2 mol %) tritiated water, and the product isolated as the 3-phenylsemicarbazone. Acetaldehyde added to a similar solution was also derivatized under identical conditions. The radioactivity of both derivatives was determined and that due to exchange in the acetaldehyde (12% of the total) subtracted, as a correction, from the activity of the material formed from the ethyl vinyl ether. From the corrected activity, κ_H/κ_T, defined as $((RH)/(RT))_{prod}((T)/(H))_{M_2O}$,[2] was obtained. They were 17.2, 19.7, and 18.8, averaging to 18.6. There is no reason to expect an uncertainty greater than the experimental scatter, 1.0, in this value.

Table I. Ethyl Vinyl Ether Cleavage in H_2O–DMSO Mixtures at 25°

Vol % DMSO	Mol % DMSO	k_2,[a] M^{-1} sec^{-1}	B
0	0	1.77	
16	4.5	1.29	
40	15.0	7.0×10^{-1}	
58	26.9	1.92×10^{-1}	
75	43.8	5.46×10^{-2}	0.45
90	69.8	3.92×10^{-2}	0.95
95	82.8	4.30×10^{-2}	2.1
98	92.5	5.28×10^{-2}	3.2
99	96.1	5.50×10^{-2}	3.9
95[b]	82.8	1.86×10^{-2}	2.0

[a] The estimated uncertainty in k_2 obtained by extrapolation in no case was greater than ±5%. [b] D_2O.

Discussion

The competitive isotope effect in 95% DMSO implies that proton transfer is rate determining in that solvent, as it is in water.[2] In sufficiently low concentrations of water it is likely that reaction of $CH_3CH{=}OC_2H_5^+$ with water would become rate determining with the result that the rate would begin to fall below expectations based on higher concentrations. Figure 4, shows that k_2 closely parallels protonated indicator dissociation constants, K_{HA}, in dilute HCl solutions.[9] Very much lower water concentrations are believed necessary to observe a change in the rate-determining step. In the remainder of this paper it is assumed that the general features of the mechanism in water,[2] and particularly the rate-determining proton transfer, are retained in all the water–DMSO mixtures here considered.

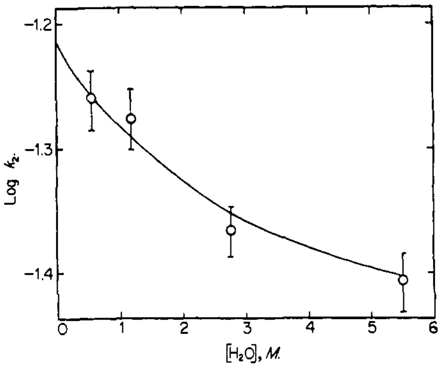

Figure 5. Effect of (H_2O) on k_2. The line was calculated with k_H, 6.1×10^{-2} M^{-1} sec^{-1}, and k_{H_3O}, 2.9×10^{-2} M^{-1} sec^{-1}; K_H was used to evaluate $(H^+)/(H^+ \cdot H_2O)$. The circles are experimental points and the vertical bars indicate a 5% uncertainty. A solution 5.5 M in H_2O has 70 mol % DMSO.

It is interesting to note that the rate of the present reaction, of the A-SE2 type, shows a pattern of changes in DMSO–H_2O mixtures which is thought characteristic of A1 reactions, and quite different from the pattern generated by A2 reactions.[10] If this is general it is particularly useful, as A-SE2 reactions can usually be distinguished from A1 reactions, quite straightforwardly, by the observation of general acid catalysis and by the magnitude of the solvent isotope effect,[11] but distinguishing them from A2 reactions can be harder.

It is not obvious why the A1 and A-SE2 reactions should behave similarly, but it is clear that A-SE2 reactions will be less favored by a DMSO medium than A2 reactions. An A2 reaction depends on the nucleophilicity of water, and DMSO is well known as a solvent which enhances nucleophilicity by virtue of its tendency to be a hydrogen bond acceptor, but not a donor.[12]

Molecularity with Respect to Water. In the range of H_2O concentrations where eq 3 is applicable, it might be expected that k_2 would be given by eq 5 if n, in Figure 1, is zero. The chemical species are those

$$C_a k_2 = k_H(H^+) + k_{H_3O}(H^+ \cdot H_2O) \qquad (5)$$

referred to in eq 2, evaluated using 0.39 for K_H; their coefficients are rate constants invariant with the solvent composition. If a mechanism in which $n > 0$ is favored

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[9] R. K. Wolford, *J. Phys. Chem.*, **68**, 3392 (1964).

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k_{H_3O} should be much greater than k_H. Also eq 5 might be expected to break down well below 1.5 M H_2O because of the large rate constants that would accompany even small concentrations of higher hydrates. In fact, as shown in Figure 5, eq 5 describes k_2 without large discrepancies up to much larger water concentration and k_{H_3O}, 2.9×10^{-2} M^{-1} sec^{-1}, is substantially *smaller* than k_H, 6.1×10^{-2} M^{-1} sec^{-1}. These results leave little doubt that an anhydrous transition state ($n = 0$) is *not* of paricularly high free energy in DMSO solution.

Isotope Effects. The observed isotope effects are averages over reactions of H^+, $H^+ \cdot H_2O$, and, perhaps higher hydrates. However some dissection to give the isotope effects on composition-invariant rate constants is possible with the help of certain reasonable approximations. If it is assumed that k_{H_3O}/k_{D_3O} has the same value, 3.2, as the over-all kinetic isotope effect in water,[2] then k_{D_3O} has the value 9.2×10^{-3} M^{-1} sec^{-1}. This can be combined with k_2 in 17.2 mol % D_2O to give a value of 2.8×10^{-2} M^{-1} sec^{-1} for k_D, from which k_H/k_D becomes 2.2. The assumption about k_{H_3O}/k_{D_3O} is not exact, because it ignores isotope effects originating outside the M_3O^+ unit in aqueous solution. However, a similar assumption leads to an isotopic α in reasonable accord with the Brønsted α,[2] suggesting that it is not in serious error. The assignment of the value, 4.2, to k_{H_3O}/k_{D_3O}, instead of 3.2, leads to a value of 2.0 for k_H/k_D, while k_H/k_D becomes 2.4 if k_{H_3O}/k_{D_3O} is 2.2.

In a solution with two proton donors the tritium content of the product is governed by eq 6.[13] The quantity $(\kappa_H/\kappa_T)_M$ is analogous to κ_H/κ_T except that it refers only to that product resulting from reaction with M^+. (The symbol M is used to indicate one of the isotopes of hydrogen without specifying which.)

$$\left(\frac{(RT)}{(RH)}\right)_{prod} = \left\{\frac{k_H(H^+)(\kappa_T/\kappa_H)_M + k_{HA}(HA)\kappa_{TA}/\kappa_{HA}}{k_H(H^+) + k_{HA}(HA)}\right\}\left(\frac{(T)}{(H)}\right)_{M_2O} \qquad (6)$$

Substituting κ_H/κ_T for $((RH)/(RT))_{prod}((T)/(H))_{M_2O}$, $H^+ \cdot H_2O$ for HA, k_{H_3O} for k_{HA}, and assuming that κ_{HA}/κ_{TA} has the same value (16.7) as κ_H/κ_T in water,[2] the value 20 ± 2 is obtained for $(\kappa_H/\kappa_T)_M$ in DMSO. By use of the Swain–Schaad relations[14] (which have been shown accurate for ethyl vinyl ether hydrolysis in water[2]) a value of 8 ± 1 is obtained for $(\kappa_H/\kappa_D)_M$ in DMSO.

The primary kinetic isotope effect, $(k_H/k_D)_I$[11] can be obtained from $(\kappa_H/\kappa_D)_M$ by means of eq 7 if l, the equilibrium constant for eq 9, is known, since $((D)/(H))_M((H)/(D))_{M_2O}$ is given by eq 8[15] and the dissociation constants are known. Assuming the aqueous solution

$$(k_H/k_D)_I = (\kappa_H/\kappa_D)_M((D)/(H))_M((H)/(D))_{M_2O} \qquad (7)$$

$$((D)/(H))_M((H)/(D))_{M_2O} = l^3K_H/K_D \qquad (8)$$

$$H_{M_3O} + D_{M_2O} \overset{l}{\rightleftharpoons} H_{M_2O} + D_{M_3O} \qquad (9)$$

value of l, 0.69,[11,15–17] a value of 3.1 is obtained for $(k_H/k_D)_I$. Since there is no obvious source of secondary solvent isotope effect for the DMSO solvated proton, $(k_H/k_D)_I$ should be the same as k_H/k_D, 2.2. Considering the long chain of calculations and the number of approximations necessary to made the comparison the agreement is considered satisfactory.

Since κ_H/κ_D is the equilibrium constant for eq 10,

$$D_{\ddagger} + H_{M_2O} \overset{\kappa H/\kappa D}{\rightleftharpoons} H_{\ddagger} + D_{M_2O} \qquad (10)$$

where $D_{\ddagger}$ and $H_{\ddagger}$ are the transition states with D and H transferring, respectively, its maximum value may be estimated with the aid of the "one frequency approximation."[18] The stretching frequency of H_2O dissolved in DMSO appears to be around 3400 cm^{-1}, as it is in liquid water. This leads to an estimate of 10 as the maximum value of κ_H/κ_D. The observed value, 7.6, obtained by applying the Swain–Schaad relation[14] to κ_H/κ_T, is close to this, suggesting that proton transfer is the major component of the reaction coordinate, as it is in water.[2]

Comparison with the Mechanism in Water. The conclusion that n is zero in DMSO has no necessary bearing on the mechanism in water. Several arguments suggest, however, that it can be carried over.

(1) There is evidence[19] that the DMSO-solvated proton is hydrogen bonded to its nearest neighbor DMSO molecule at least as strongly as the H_3O^+ unit of the aquated proton is hydrogen bonded to its nearest neighbor water molecules. If one of the DMSO molecules can be displaced by a substrate molecule there is no obvious reason that a water molecule cannot also be displaced.

(2) One of the original reasons for suggesting an indirect transfer ($n \neq 0$) was the high heat of hydration of the H_3O^+ unit (100 kcal mol^{-1}).[20,21] It was thought that the removal of any one of the three water molecules hydrogen bonded to the H_3O^+ unit would be endothermic by about one-third of this amount. However, recent gas-phase studies of this system[22] suggest that the endothermicity is strongly progressive. The removal of one water molecule from $H_9O_4^+$ in the gas phase has $\Delta H^\circ = 17$ kcal mol^{-1}.[22] In aqueous solution the value would be substantially less because of the possibility of compensation by strengthening other hydrogen bonds. Such a value no longer provides strong support for a mechanism with $n \neq 0$.

(3) The isotope effects in DMSO appear to be similar to those in water, except for (k_H/k_D).[2] The latter is low in DMSO because of the low zero-point energy of the DMSO solvated proton,[19] rather than because of any change in the transition state structure. Calculations based on the use of isotope effects in water to evaluate those on $H^+ \cdot H_2O$ terms in DMSO are quite reasonably successful. None of this supports a

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drastic change of mechanism on going from DMSO to H_2O as solvent.

Experimental Section

Materials. Ethyl vinyl ether and dimethyl sulfoxide were obtained commercially and were purified by distillation. The latter was stored under dry nitrogen after distillation at 0.2 mm from calcium hydride. Standard hydrochloric acid and sodium hydroxide solutions were prepared in the usual manner.[23] Deuterium chloride was prepared from benzoyl chloride and D_2O.[24] The acidified aqueous dimethyl sulfoxide solutions were prepared gravimetrically. Each reaction mixture was titrated potentiometrically for acid after the completion of measurements.

Isotopic Product Studies. Each product collection with ethyl vinyl ether as a substrate was accompanied by one in which acetaldehyde itself was used as substrate under otherwise identical conditions. In a typical experiment a solution of 0.6 ml of ethyl vinyl ether (or 0.35 ml of acetaldehyde) in 40 ml of aqueous DMSO (5 ml of H_2O/100 ml of solution) containing 9.1×10^{-3} *M* HCl and -10^{-2} mCi of tritium was maintained at 25° for 4.5 hr. The reaction mixture was added to 0.8 g of 4-phenylsemicarbazide and allowed to stand at 25° for 1 hr. Dilution with 200 ml of H_2O and chilling induced crystallization. The white needles were filtered and recrystallized from aqueous methanol (mp 147.5–148.5°, lit.[2,25] mp 151–152°). Before addition of the substrate a small portion of the aqueous DMSO had been set aside for later counting. The semicarbazone products and the aqueous DMSO were analyzed for tritium.[26] The correction for the incorporation of tritium by the acetaldehyde by exchange is given in eq 11. The subscripts

$$\frac{r_e}{n_e} = \left[\frac{r_a/t_a}{n_a}\right]\left[t_e - \frac{1 - \exp\{k_2(\mathrm{H}^+)t_e\}}{k_2(\mathrm{H}^+)}\right] \qquad (11)$$

a and e refer to acetaldehyde and vinyl ether experiments, respectively. The counting rate due to exchange is *r*. (This is the total counting rate in the case of r_a.) The incubation period is *t*, and *n* is the number of moles of derivative counted.

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Anomalous Reactions of Bis(trifluoromethyl)diazomethane and Bis(trifluoromethyl)diazirine with Saturated Hydrocarbons[1]

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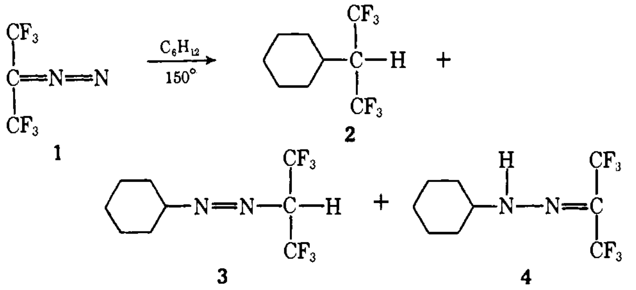
Abstract: Bis(trifluoromethyl)diazomethane (**1**) reacted anomalously with cyclohexane to give a hydrazone (**4**) and an azo compound (**3**) as the major products in addition to the expected carbene insertion product (**2**). Evidence for a radical chain mechanism is presented. Bis(trifluoromethyl)diazirine (**8**) also reacted abnormally with cyclohexane, but the major product was an unexpected imine (**9**) rather than the adducts obtained with bis(trifluoromethyl)diazomethane. Hexafluoroacetone azine (**14**) gave the normal insertion product (**2**) with cyclohexane. Reactions with other hydrocarbons are discussed in light of possible mechanisms.

The thermal reactions of aliphatic and aromatic diazo compounds with saturated hydrocarbons have been intensively investigated.[2] Such reactions normally give carbene insertion products and are frequently used to help establish the reactivity of the intermediate carbene. In no case have other primary products derived from the diazo compound and the saturated hydrocarbon been reported. This also appears to be true of the reactions of diazirines (cyclic diazo compounds) with saturated hydrocarbons, although these compounds have been less thoroughly investigated.[3]

We have found that unexpected reactions occur when either bis(trifluoromethyl)diazomethane (**1**)[4] or its cyclic isomer, bis(trifluoromethyl)diazirine (**8**)[4] is heated with a saturated hydrocarbon.

Bis(trifluoromethyl)diazomethane (1). When **1** was heated at 150° for 8 hr in excess cyclohexane, only a small amount of the expected carbene insertion product, [2,2,2-trifluoro-1-(trifluoromethyl)ethyl]cyclohexane (**2**), was obtained. The major products were an azo compound (**3**) and a hydrazone (**4**) (95% combined yield of **2**, **3**, and **4**). These addition products of the diazo compound **1** with cyclohexane were obtained even though the reaction was run at a temperature shown to be sufficiently high to generate a carbene, from **1**.[4]



The structures of the products suggested that adducts **3** and **4** were formed from a common intermediate by the radical chain mechanism given by reactions 1–3. Additional experiments were conducted to test this

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