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## The Transition State in Methyl Radical Formation. The Secondary $\alpha$ -Deuterium Isotope Effect<sup>1</sup>

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The secondary  $\alpha$ -deuterium isotope effect was determined for the unimolecular formation of methyl and methyl- $d_3$  radicals and acetophenone from methyltrideuteriomethylphenylcarbonyl hypochlorite.  $k_H/k_D$  varied from 1.17 at  $-9^\circ$  to 1.12 at  $75^\circ$ . From the temperature dependence of the effect it was concluded that the transition state is more akin to products than to the reactant oxy radical.

The study of isotope effects on reaction rates and chemical equilibria has developed into a valuable mechanistic tool.<sup>2</sup> Substitution of deuterium on a reacting carbon atom leads to a decrease in the rate of SN1 reactions. This secondary  $\alpha$ -deuterium isotope effect has been found to result in  $k_H/k_D \cong 1.15$  per deuterium for a considerable number of "limiting" solvolytic reactions.<sup>3,4</sup>

The generally accepted interpretation of secondary  $\alpha$ -deuterium effects is based on Bigeleisen's equation for the effect of isotope substitution on reaction rates.<sup>5</sup> The theoretical treatment is based on absolute rate theory and statistical mechanics; anharmonicity is neglected. Although absolute rate theory predicts reaction rates only qualitatively, the effect of isotopic substitution on the various quantities can be calculated with much greater reliability than the quantities themselves. Streitwieser has adapted the general equation to secondary  $\alpha$ -effects<sup>6</sup> and by a series of reasonable approximations has reduced it to a form similar to eq. 1.

$$k_H/k_D = be^{hc \sum_i [(\omega_{H_i} - \omega_{D_i}) - (\omega_{H_i}^* - \omega_{D_i}^*)]/2kT} \quad (1)$$

In this equation the pre-exponential term  $b$  is not a strictly temperature-independent term, but at the temperatures usually employed in mechanistic work it remains fairly constant and is usually close to unity (*vide infra*);  $\omega_i$  are the fundamental frequencies in  $\text{cm}^{-1}$ ; \* denotes the transition state.

For the stretching and bending frequencies,  $\omega_D = \omega_H/1.31$  is a good approximation<sup>7</sup>; substitution in eq. 1 and insertion of the values of the constants lead to eq. 2.

$$k_H/k_D = be^{0.170 \sum_i (\omega_{H_i} - \omega_{H_i}^*)/T} \quad (2)$$

Thus the isotope effect is related to changes in vibrational frequencies from starting to transition state; herein lies the value of secondary  $\alpha$ -effects as a mechanistic tool. A net decrease in the sum of the frequency changes leads to a normal effect,  $k_H/k_D > 1$ . In reactions accompanied by an  $sp^3$ - toward  $sp^2$ -hybridization

change the stretching and one of the bending frequencies do not change much; the bending frequency which eventually becomes the out-of-plane bending mode in the  $sp^2$ -hybrid decreases by about  $500 \text{ cm}^{-1}$  for the complete change and is considered the major contributor to the isotope effect.<sup>8</sup> Since similar hybridization changes accompany SN1 and radical reactions, similar isotope effects of about 15% are to be expected for both,<sup>9b</sup> and the secondary  $\alpha$ -deuterium effect has been determined in mechanistic studies of thermal cleavage, radical addition, Diels-Alder, and cycloaddition reactions.<sup>9</sup> For a fully formed carbonium ion in the transition state an isotope effect of  $k_H/k_D = 1.4$  has been calculated by an equation similar to 2<sup>6</sup>; the lower observed value of  $\sim 1.15$  indicates that, as would be expected, the reacting carbon atom has not fully attained a tricoordinated  $sp^2$ -structure in the transition state.

This universal pattern of  $k_H/k_D \cong 1.15$  per deuterium for unimolecular reactions involving hybridization changes from  $sp^3$  to  $sp^2$  has been violated by the report of an inverse effect,  $k_H/k_D = 0.92$  for three deuterium atoms, in the rate of methyl radical formation by gas phase pyrolysis of dimethylmercury.<sup>10</sup> This violation of the empirical pattern has led to a questioning of the validity of conclusions drawn from studies of  $\alpha$ -deuterium effects.<sup>11</sup>

The present paper reports a study of the  $\alpha$ -deuterium kinetic isotope effect in the formation of methyl radicals by carbon-carbon bond cleavage in solution, the temperature dependence of the effect, and the magnitude of the pre-exponential factor in eq. 2. We also offer a possible explanation for the unexpected dimethylmercury results.

### Results and Discussion

We undertook the determination of the  $\alpha$ -deuterium kinetic isotope effect in the formation of methyl radicals from methyltrideuteriomethylphenylcarbonyl hypochlorite whose decomposition has been studied.<sup>12</sup> In nonpolar solvents and in the presence of reactive hydrogen sources, hypochlorites of this type react by a radical chain reaction, initiated by light or other radical

(1) Research was performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955); (b) F. H. Westheimer, *ibid.*, **61**, 265 (1961).

(3) R. E. Weston, *Ann. Rev. Nucl. Sci.*, **11**, 439 (1961).

(4) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 170 ff.

(5) (a) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949); (b) J. Bigeleisen and M. Wolfsberg, "Advances in Chemical Physics," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958, p. 15.

(6) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Susuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

(7) The value 1.31 is a weighted average of the ratio of the fundamental frequencies in the methyl and methyl- $d_3$  halides [A. D. Dickson, *et al.*, *J. Chem. Phys.*, **27**, 445 (1957)] and in  $\text{C}_2\text{H}_5\text{Br}$  and  $\text{C}_2\text{D}_5\text{Br}$ ; the bending frequencies have been weighted more heavily as in ref. 8.

(8) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 1861 (1961).

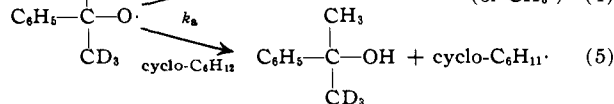
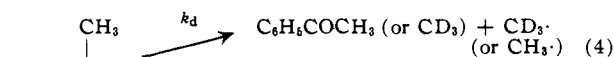
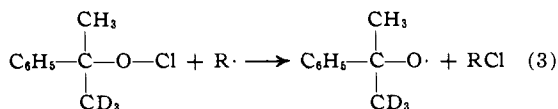
(9) (a) S. Seltzer, *ibid.*, **83**, 2625 (1961); (b) *ibid.*, **85**, 14 (1963); (c) *ibid.*, **85**, 1360 (1963); (d) D. B. Denney and N. Tunkel, *Chem. Ind. (London)*, 1383 (1959); (e) D. E. Van Sickle, *Tetrahedron Letters*, No. 19, 687 (1961); (f) M. Takahasi and R. J. Cvetanović, *Can. J. Chem.*, **40**, 1037 (1962); (g) M. Feld, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 4451 (1962); (h) T. J. Katz and R. Dessau, *ibid.*, **85**, 2172 (1963).

(10) R. E. Weston and S. Seltzer, *J. Phys. Chem.*, **66**, 2192 (1962).

(11) M. J. Goldstein and G. L. Thayer, Jr., *J. Am. Chem. Soc.*, **85**, 2679 (1963).

(12) (a) C. Walling and A. Padwa, *ibid.*, **85**, 1593 (1963). We thank Professor Walling for suggesting this particular hypochlorite. (b) M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 748 (1950).

initiators<sup>13</sup> as shown in eq. 3-5. Cyclohexane was used as the reactive hydrogen source.



Chain lengths are long; a minimum of  $10^4$  has been established for *t*-butyl hypochlorite.<sup>13</sup> The methyl radicals produced according to eq. 4 attack unreacted hypochlorite to give  $\text{CH}_3\text{Cl}$  (or  $\text{CD}_3\text{Cl}$ ) and regenerate oxy radicals. Cyclohexyl radicals (eq. 5) react in the same fashion. The ratio of  $\text{CH}_3\text{Cl}$  to  $\text{CD}_3\text{Cl}$  formed is the ratio of the rate constants for C- $\text{CH}_3$  and C- $\text{CD}_3$  bond cleavage, *i.e.*,  $k_{\text{H}}/k_{\text{D}}$  for three deuterium atoms. The fragmentation is a unimolecular thermal reaction<sup>14</sup> although light was used to initiate the over-all reaction. Possible side reactions that could complicate the handling of the data were investigated with dimethylphenylcarbinyl hypochlorite (cumyl hypochlorite). The cumyloxy radical can abstract a hydrogen from the methyl groups of unreacted hypochlorite. This abstraction will be accompanied by a considerable primary isotope effect<sup>15</sup>; this would lead to preferential destruction of the methyl group, compared to methyl- $d_3$ , on unreacted hypochlorite. Such methyl hydrogen abstraction leads to the formation of methylchloromethylphenylcarbinyl hypochlorite and, after reaction and fragmentation, to methylene chloride; chloromethyl is at least three times better as a leaving group in the fragmentation than methyl.<sup>12a</sup> We found that in the presence of a twofold excess of cyclohexane over hypochlorite, as dilute solutions in carbon tetrachloride, the yield of methylene chloride was a negligible 0.1% at 75°. The extent of methyl hydrogen abstraction at lower temperatures was not determined, but it is expected to decrease because of increased selectivity of oxy radicals at lower temperatures. A twofold excess of cyclohexane was used in all isotope effect determinations. Another side reaction, cleavage of the cumyloxy radical to acetone and phenyl radical, occurs to the extent of 2% but does not interfere with the ratio  $\text{CH}_3\text{Cl}/\text{CD}_3\text{Cl}$ .

The hypochlorite was prepared *via* the alcohol from acetophenone- $d_3$  and methylmagnesium iodide. The possibility of deuterium exchange during acid hydrolysis<sup>16</sup> of  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{CD}_3)\text{OMgI}$  was investigated by n.m.r. and none was found. Analysis of the alcohol for deuterium content showed greater than 99% deuteration of one methyl group: Treatment of the alcohol with  $\text{HOCl}$  gave the hypochlorite; no deuterium exchange is expected at the acidity level of the  $\text{HOCl}$  treatment of the alcohol. Mass spectrometry indicated that 1.3% of the deuterated methyl is  $-\text{CD}_2\text{H}$  and all data were corrected accordingly.

<sup>13</sup> C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

<sup>14</sup> A. L. Williams, E. A. Overgitt, and J. W. Brooks, *ibid.*, **78**, 190 (1956); P. Grey and A. L. Williams, *Trans. Faraday Soc.*, **55**, 760 (1959).

<sup>15</sup> D. B. Denney, D. Z. Denney, and G. Feig, *Tetrahedron Letters*, No. 15, 19 (1959).

<sup>16</sup> V. N. Setkina and D. N. Kursanov, *Izvest. Acad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 433 (1959); *Chem. Abstr.*, **53**, 1803b (1959).

The  $\text{CH}_3\text{Cl}/\text{CD}_3\text{Cl}$  ratio was determined by mass spectrometry. We used the 52 and 55 peaks. A consolidated-Nier mass spectrometer was used as a single collector, and it was calibrated with known mixtures for its relative sensitivity to the two compounds. The correction factor to be applied to the 52/55 ratio was  $0.99 \pm 0.01$ . A correction factor of 1.45 has been reported for the ratio of the parent peaks, 50/53.<sup>17</sup> We find  $1.00 \pm 0.04$  for this ratio. Similar sensitivities for the two compounds are expected *a priori* and the fragmentation patterns (Table I) of the two compounds are very similar, after allowance for the different masses involved.

TABLE I  
MASS SPECTRAL FRAGMENTATION PATTERNS

| <i>m/e</i> | $\text{CD}_3\text{Cl}^a$ | $\text{CH}_3\text{Cl}$ | $\text{CH}_3\text{Cl}^b$ |
|------------|--------------------------|------------------------|--------------------------|
| 47         | 4.3                      | 7.7                    | 7.8                      |
| 48         | 0.06                     | 3.5                    | 3.5                      |
| 49         | 4.02                     | 10.0                   | 10.0                     |
| 50         | 0.25                     | 100.0                  | 100.0                    |
| 51         | 8.01                     | 3.52                   | 3.38                     |
| 52         | 1.23                     | 31.6                   | 31.5                     |
| 53         | 100                      | 0.43                   | 0.34                     |
| 54         | 1.44                     |                        |                          |
| 55         | 31.1                     |                        |                          |
| 56         | 0.39                     |                        |                          |

<sup>a</sup> From which 1.3%  $\text{CD}_2\text{HCl}$  was deduced to be present.

<sup>b</sup> A.P.I. Research Project 44, Mass Spectral Data, Carnegie Institute of Technology, Pittsburgh 13, Pa.

The isotope effect was determined over a range of 84° and the results are shown in Table II. The constant temperature baths were controlled to within 0.5°. The ratio  $k_{\text{H}}/k_{\text{D}}$  per deuterium is the cubic root of  $\text{CH}_3\text{Cl}/\text{CD}_3\text{Cl}$  after correction for relative sensitivities and the presence of  $-\text{CD}_2\text{H}$ ; secondary  $\alpha$ -effects would be expected to be very nearly cumulative although some  $\beta$ -effects are not, apparently because of conformational requirements.<sup>18</sup>

TABLE II  
KINETIC  $\alpha$ -DEUTERIUM ISOTOPE EFFECT ON FORMATION OF METHYL RADICAL

| <i>t</i> , °C. | Solvent                           | $\text{CH}_3\text{Cl}/\text{CD}_3\text{Cl}^a$ | $k_{\text{H}}/k_{\text{D}}^b$ |
|----------------|-----------------------------------|---|-------------------------------|
| -9             | $\text{CCl}_4$                    | $1.588 \pm 0.006$                             | $1.163 \pm 0.01$              |
| 20             | $\text{CCl}_4$                    | $1.486 \pm .003$                              | $1.137 \pm .01$               |
| 50             | $\text{CCl}_4$                    | $1.429 \pm .009$                              | $1.123 \pm .01$               |
| 75             | $\text{CCl}_4$                    | $1.401 \pm .006$                              | $1.115 \pm .01$               |
| -9             | $\text{CH}_3\text{CN}^c$          | 1.598   | 1.165                         |
| -7             | $\text{C}_6\text{H}_6^c$          | 1.584   | 1.162                         |
| -7             | $\text{C}_6\text{H}_5\text{CN}^c$ | 1.571   | 1.159                         |
| -10            | $\text{CH}_3\text{COOH}^c$        | 1.618   | 1.170                         |
| 10             | $\text{CH}_3\text{COOH}^c$        | 1.518   | 1.145                         |

<sup>a</sup> Uncorrected for relative sensitivity of mass spectrometer.

<sup>b</sup> Corrected values, per deuterium. <sup>c</sup> 4.0 M in  $\text{CCl}_4$ .

These results show that the magnitude of the effect is in line with other determinations on limiting solvolyses and unimolecular thermal cleavage reactions. The observed effect also confirms the universality of the pattern of similar  $\alpha$ -effects in reactions involving similar hybridization changes, irrespectively of the type of bond cleavage, homolytic or heterolytic. The unexpected small inverse effect reported for methyl radical formation by gas phase pyrolysis of dimethylmercury<sup>10</sup> does not therefore reflect any peculiarity of the methyl radical.

<sup>17</sup> G. Ghiltz, *et al.*, *J. Chem. Phys.*, **38**, 1053 (1963).

<sup>18</sup> V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *J. Am. Chem. Soc.*, **85**, 2413 (1963).

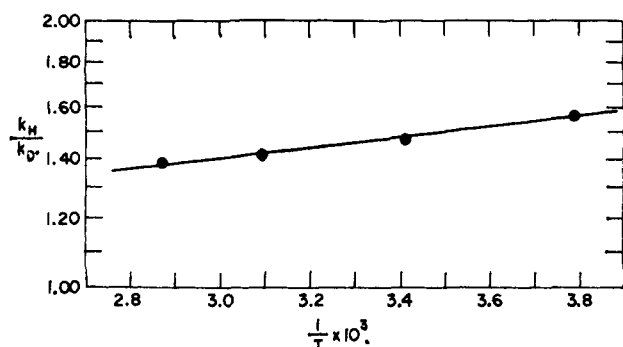


Fig. 1.—Semilog plot of  $k_H/k_D$  (for 3 D's) vs.  $1/T$  in methyl radical formation from  $C_6H_5C(CH_3)(CD_3)O\cdot$ .

The anomalous results with dimethylmercury may be misleading since no study of pressure dependence of the isotope effect was made; the effect was determined at pressures about 600 mm. For gas-phase systems a strong dependence of isotope effect on pressure has been found recently; this dependence is attributed to thermal nonequilibrium conditions at low pressure.<sup>19</sup> In the unimolecular gas-phase isomerization of  $CH_3NC$  to  $CH_3CN$ , for example,  $k_H/k_D = 0.28$  at  $10^{-2}$  mm., about 0.9 at 600 mm., and 1.07 at the high pressure limit, which probably would be the value in solution. It should be pointed out, however, that small, inverse  $\alpha$ -effects have been reported in deoxymercuration<sup>20</sup>; the nature of the transition state has not been definitely established for this type of reaction, and no precise predictions can be made for the isotope effect. The fact that mercury is involved again may or may not be significant.

A plot of  $\log(k_H/k_D)$  for three deuterium atoms vs.  $1/T$  is shown in Fig. 1. The rather good straight-line fit indicates that the pre-exponential term is fairly constant over a temperature range of  $84^\circ$ . From a least-squares treatment, the extrapolated high temperature value (the pre-exponential term  $b$ ) is  $0.93 \pm 0.02$  and from the slope a total decrease of  $811 \pm 15 \text{ cm.}^{-1}$  is calculated for the frequency changes from starting to transition state. This corresponds to a net decrease of  $270 \pm 5 \text{ cm.}^{-1}$  per deuterium atom and, to our knowledge, the only other value available for comparison is a net increase of  $375 \pm 111 \text{ cm.}^{-1}$  reported for the  $SCN^-$  catalyzed isomerization of maleic acid where the reverse hybridization changes are taking place,  $sp^2$  toward  $sp^3$  in the transition state.<sup>8,21</sup>

For the maleic acid isomerization the total net change accompanying conversion to a fully formed tetrahedral carbon was calculated as  $565 \text{ cm.}^{-1}$  and it was concluded that more than half of the vibrational changes had occurred in the transition state. In our case the C-H bond in the methyl radical is about  $0.013 \text{ \AA}$ . shorter than the bond in methane<sup>22</sup> and about equal to the bond length in ethylene. The ethylene frequencies will be taken as a model for the fully formed methyl

radical.<sup>23</sup> The average of the C-H stretching frequencies of a methyl group is about  $2920 \text{ cm.}^{-1}$  and that of olefins about  $3020 \text{ cm.}^{-1}$ . For the methyl group the symmetrical and asymmetrical C-H deformations occur around  $1375$  and  $1450 \text{ cm.}^{-1}$ , respectively. Although specific assignments are difficult to make in a complicated intermediate such as cumyloxy radical, we obtained two strong bands at  $1375$  and  $1448 \text{ cm.}^{-1}$  in cumyl hypochlorite.

The asymmetrical deformation frequency in the series methyl chloride, bromide, iodide, decreases by a factor of 1.37 in the deuterated analogs, the symmetrical by a factor of 1.31.<sup>24</sup> Such a decrease in the deuterated cumyl hypochlorite would bring the asymmetrical deformation to  $1057$  and the symmetrical to  $1050 \text{ cm.}^{-1}$ . The deuterated compound shows a strong band at  $1050 \text{ cm.}^{-1}$  with a definite shoulder; such a band is absent in the natural compound. We take the average of the deformation frequencies as  $1412 \text{ cm.}^{-1}$ . The C-H in-plane bend of ethylenes is about  $1415 \text{ cm.}^{-1}$ ; the out-of-plane bend of vinyl- $CH_2$  is about  $910 \text{ cm.}^{-1}$ . The total frequency changes for the methyl hydrogens from starting state (oxy radical) to a fully formed methyl radical are from  $2920$  to  $3020 \text{ cm.}^{-1}$  (stretching), no change in the deformation frequency that becomes the in-plane bend, and from  $1412$  to  $910 \text{ cm.}^{-1}$  for the deformation that becomes the out-of-plane bend. The total net frequency change from tetrahedral to a fully formed methyl radical is then about  $400 \text{ cm.}^{-1}$ ; the experimentally determined change of  $270 \text{ cm.}^{-1}$  from starting to transition state indicates that well over half of the vibrational changes accompanying the formation of the methyl radical have occurred in the transition state. The conclusion that the transition state is more akin to products than to reactants in a reaction involving carbon-carbon bond cleavage and the formation of a methyl radical and a double bond is consistent with the findings of Szwarc and co-workers.<sup>25</sup> They have concluded that the transition state for methyl radical addition to olefins, a reaction similar to the reverse of cumyloxy decomposition, is closer to the configuration of the reactants than to that of products.

The energetics of the reaction show that  $\beta$ -scission of the oxy radical requires a considerable energy of activation, even though the reactant is a high energy intermediate. From the temperature dependence of the ratio of the rate constants for abstraction and decomposition,  $k_a/k_d$  (eq. 4, 5), we calculate  $E_{a,dec} - E_{a,abs} = 5 \text{ kcal./mole}$ <sup>26</sup> (Table III, no. 1 and 2). The energy of activation for  $\beta$ -scission of the *t*-butoxy radical is estimated to be  $13 \text{ kcal./mole}$  in the gas phase.<sup>27</sup> Assuming a similar value in  $CCl_4$  and with  $E_{a,dec} - E_{a,abs} = 10 \text{ kcal./mole}$  for the *t*-butoxy radical toward cyclohexane<sup>12a</sup> we obtain  $E_{a,abs} = 3 \text{ kcal./mole}$ . The energy of activation for hydrogen abstraction must be about the same for all *t*-alkoxy radicals since they exhibit similar selectivities and the same type bonds are involved.

(19) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **85**, 2365 (1963), and references therein.

(20) M. M. Kreevoy and B. M. Eisen, *J. Org. Chem.*, **28**, 2104 (1963).

(21) The secondary  $\alpha$ -deuterium isotope effect has been measured for the iodide-promoted debromination of *sym*-tetrabromoethane- $d_2$  as a function of temperature [W. G. Lee and S. I. Miller, *J. Phys. Chem.*, **66**, 655 (1962)]. The isotope effect was observed to decrease with increasing temperature.

(22) (a) C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, **30**, 774 (1959);

(b) G. Herzberg, *Proc. Roy. Soc. (London)*, **A262**, 291 (1961).

(23) Infrared frequencies from: L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 13, 34.

(24) A. D. Dickson, I. M. Mills, and B. Crawford, *J. Chem. Phys.*, **27**, 445 (1957).

(25) M. Feld, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 4451 (1962).

(26) This value compares with  $5.1 \text{ kcal./mole}$  reported in ref. 12a.

(27) P. Grey and A. L. Williams, *Chem. Rev.*, **89**, 239 (1959).

This leads to a value of  $E_{a,dec} \cong 8$  kcal./mole, a considerable energy in excess of that of the reactive cumyloxy radical. This is compatible with the substantial reorganization of the bonds indicated by the  $\alpha$ -deuterium effect.

TABLE III

| $k_a/k_d$ FOR CUMYL HYPOCHLORITE WITH CYCLOHEXANE |                      |  |                   |
|---|----------------------|--|-------------------|
| No.   | $t, ^\circ\text{C.}$ | Solvent                                | $k_a/k_d$         |
| 1   | 75                   | $\text{CCl}_4$                         | 1.3 <sup>a</sup>  |
| 2   | 40                   | $\text{CCl}_4$                         | 2.87 <sup>c</sup> |
| 3   | 40                   | 6.12 M $\text{CH}_3\text{COOH}^b$      | 1.12 <sup>c</sup> |
| 4   | 40                   | 4.90 M $(\text{CH}_3)_3\text{CCOOH}^b$ | 2.04 <sup>c</sup> |

<sup>a</sup> 0.5 M hypochlorite, 1.5 M cyclohexane. <sup>b</sup> In  $\text{CCl}_4$ . <sup>c</sup> 0.5 M hypochlorite, 1.0 M cyclohexane.

A direct comparison of the magnitude of the isotope effect with effects reported for other systems is not meaningful at this stage because the pre-exponential terms for most other systems are not known and, especially, the significance of inductive effects is not yet clear. A greater inductive effect is attributed to deuterium than to hydrogen<sup>28</sup>; this effect is caused by the anharmonic character of the normal vibrations. Basicities of deuterium-substituted acids have been explained by a greater inductive effect of deuterium.<sup>29</sup> Substitution of deuterium in the  $\alpha$ -position of a carbonium ion would be expected to increase stability, on this basis. It has therefore been suggested that the usual  $\sim 15\%$  decrease in the rate of limiting solvolyses of  $\alpha$ -deuterated compounds and associated with coordination number or hybridization changes would be still greater were it not for this superposed inductive effect.<sup>29</sup> The  $\alpha$ -deuterium effect on the rate of carbanion formation is again  $\sim 15\%$  even though inductive and hybridization effects are now acting in the same direction.<sup>30</sup> In methyl radical formation the significance of inductive effects would be minimal, but the over-all effect is again  $\sim 15\%$ . It appears that, without independent knowledge of the exact position of the transition state along the reaction coordinate, no estimate can be made of the significance of the  $\alpha$ -deuterium inductive effect from the isotope effect. The isotope effect is the result of changes in the C-H and C-D force constants and cannot be separated into inductive and vibrational components.<sup>31</sup>

It should be noted that the extrapolated high temperature value of  $0.93 \pm 0.02$  for three deuterium atoms (the pre-exponential term) is not the high temperature limit of the isotope effect; as noted earlier, the pre-exponential term is not temperature independent. The theoretical treatment upon which eq. 2 is based requires the high temperature limit of the isotope effect to equal  $\nu_{L,H^*}/\nu_{L,D^*}$  (1.08 for our compound)<sup>32</sup> and this has been found to be the case at temperatures about  $1000^\circ\text{K.}$ <sup>17,33</sup> For unimolecular cleavage of compounds of the type  $\text{CH}_3\text{-X}$ , where X is a heavy atom or group, calculations show that an extrapolated value of about 0.95 is to be expected for the

(28) E. A. Halevi, *Tetrahedron*, **1**, 174 (1957).

(29) A. Streitweiser, Jr., and H. S. Klein, *J. Am. Chem. Soc.*, **85**, 2759 (1963).

(30) A. Streitweiser, Jr., and D. E. Van Sickle, *ibid.*, **84**, 254 (1962).

(31) For a fuller discussion of this point see: R. E. Weston, *Tetrahedron*, **6**, 31 (1959).

(32) For the definition and method of calculation of the  $\nu_L$  ratio see ref. 5b.

(33) (a) H. S. Johnston and E. Tschukow-Roux, *J. Chem. Phys.*, **36**, 463 (1962); (b) T. E. Sharp and H. S. Johnston, *ibid.*, **37**, 1541 (1962).

pre-exponential term at  $20^\circ$  for a fully deuterated methyl group.<sup>34</sup>

We also thought it worthwhile to investigate complex formation by the oxy radical. Interest in and realization of the importance of complex formation in free-radical reactions is relatively recent.<sup>12a,35</sup> The *t*-butoxy radical has been found to form complexes with benzene, acetonitrile, acetic acid, etc.<sup>35b</sup>; complexing results in smaller  $k_a/k_d$  ratios, *i.e.*, decomposition by  $\beta$ -scission is favored. Table III, no. 3 and 4, shows the effect of acetic acid and trimethylacetic acid on  $k_a/k_d$ . In an attempt to determine the extent of involvement of the methyl groups of the oxy radical in the complex, we investigated the effect of the presence of radical-complexing agents on the isotope effect. If in the complex there develops some degree of steric repulsion between a methyl group and the complexing agent, then because of the difference in volume between a  $\text{CH}_3$ - and  $\text{CD}_3$ - group there might be a different preference ( $k_H/k_D$ ) of bond ruptures when compared to the non-complexed system.<sup>36</sup> Table II shows that the presence of acetic acid, acetonitrile, benzene, and benzonitrile does not alter the isotope effect. We take this to indicate that the methyl groups in the equilibrium complex or the incipient methyl radical in the transition state are not being sterically compressed to any large extent during reaction, nor does the expansion caused by the stretching of the C-C bond create any severe steric interaction with the complexing agent.

### Experimental

**Methyltrideuteriomethylphenylcarbinyl Hypochlorite.**—Freshly distilled methyl iodide (11.0 g., 0.077 mole) in 100 cc. of dry ether was slowly added to 1.80 g. (0.074 g.-atom) of magnesium turnings. Upon complete reaction, 5.0 g. (0.045 mole) acetophenone-*d*<sub>2</sub> (Merck and Co., Ltd.) in 40 cc. of dry ether was added dropwise and the mixture was refluxed for an additional 0.5 hr. The magnesium salt was hydrolyzed with 6 cc. of 96% sulfuric acid in 175 g. of ice. The organic layer was separated and washed with 25 cc. of saturated aqueous sodium chloride solution, twice with 25 cc. of saturated sodium carbonate-sodium chloride, and three times with saturated sodium chloride solution. Removal of volatile components by aspirator-vacuum gave 4.90 g. of pale yellow-colored product. Gas-liquid chromatography (g.l.c.) on Carbowax 20M-KOH-washed Firebrick (the material cleaves on other columns) showed a minimum purity of 99%. Infrared and n.m.r. established the structure as methyltrideuteriomethylphenylcarbinol, yield 86%,  $n_D^{25}$  1.5184; for the natural material, cumyl alcohol, lit.<sup>12a</sup>  $n_D^{25}$  1.5197; n.m.r. showed  $100 \pm 2.5\%$  deuteration of one methyl group.

*Anal.* Calcd. for  $\text{C}_9\text{H}_9\text{D}_9\text{O}$ : C, 77.65; H + D, 10.85. Found: C, 77.60, 77.02; H + D, 10.85, 11.12.

The alcohol was treated with a twofold excess of 2.2 N hypochlorous acid, essentially as in ref. 12a. No exchange occurs at this acidity level (*vide infra*). The yield of hypochlorite from the alcohol was 96.4% of theoretical. Mass spectrometry of the methyl chloride evolved during light-initiated decomposition of the hypochlorite in the presence of cyclohexane showed that  $\text{CD}_2\text{HCl}$  amounted to 1.3% of  $\text{CD}_3\text{Cl}$ ; this deduction was made from the magnitude of the 54 ( $\text{CD}_2\text{HCl}^{37}$ ) peak after correction for contributions of  $\text{C}^{13}\text{D}_3\text{Cl}^{36}$  to that peak according to its fragmentation pattern. This amount of  $-\text{CD}_2\text{H}$  is consistent with the analysis and n.m.r. spectrum of the alcohol; the material with which all isotope effects were determined was taken to contain 98.7%  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{CD}_2)\text{OCl}$  and 1.3%  $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{CD}_2\text{H})$ .

(34) M. Wolfsberg and M. J. Stern, presented as paper No. SM-50/22 at the Symposium on Isotopic Mass Effects in Chemistry and Biochemistry, Vienna, Dec. 1963; to be published in *J. Pure Appl. Chem.*

(35) (a) F. F. Rust and E. A. Youngman, *J. Org. Chem.*, **27**, 3778 (1962); (b) C. Walling and P. Wagner, *J. Am. Chem. Soc.*, **85**, 2333 (1963); (c) G. A. Russell, A. Ito, and D. G. Hendry, *ibid.*, **85**, 2976 (1963).

(36) K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *ibid.*, **85**, 1199 (1963).

OCl. It was stored at 0° in the dark as a dilute solution in carbon tetrachloride. Under these conditions the hypochlorite is stable; about 1% decomposition over a period of 3 months was found by iodometric titration.

**Possible deuterium exchange** during acid hydrolysis of  $C_6H_5C(CH_3)(CD_2)OMgI$  was investigated with cumyl alcohol; 1.5 g. of the alcohol in 12.5 cc. of ether was washed with 0.6 cc. of concentrated sulfuric acid in 18 cc. of  $D_2O$ ; these conditions are similar to those of the hydrolysis of the magnesium salt. The two layers were allowed to remain in contact for 24 hr. at room temperature with occasional shaking; n.m.r. analysis showed no detectable incorporation of deuterium within experimental error,  $\pm 2.5\%$ .

**Standard mixtures** of methyl chloride and methyl- $d_3$  chloride were prepared volumetrically. Some difficulty was encountered because of the solubility of the two gases in stopcock grease, but it was overcome by the use of Cello-grease (Fisher Scientific Co.). Mixtures of varying proportions were made, and the relative sensitivity of the mass spectrometer to the two compounds was found to be independent of the composition of the mixture.

The methyl chloride used (The Matheson Co., Inc.) was purified by g.l.c. on a dinonyl phthalate 2-m. column.

**Methyl- $d_2$  chloride** was prepared from methyl- $d_3$  iodide containing 1.3% methyl- $d_2$  iodide (Merck and Co., Ltd.) by passing over a 50-fold excess of a hot mixture of aluminum chloride, mercuric chloride, and asbestos fiber under reduced pressure at 100°. Thirty passes gave almost complete conversion to the chloride. The material was purified by g.l.c. and mass spectroscopy showed that it contained 1.3% methyl- $d_2$  chloride.

**Determination of the Isotope Effect.**—A typical experiment is described. A solution of hypochlorite (0.5 M) and freshly distilled cyclohexane (1.0 M, Eastman White Label) in freshly distilled carbon tetrachloride (Baker and Adamson) was prepared in the dark. It was placed in a breakseal ampoule, wrapped in black cloth, degassed under high vacuum, sealed, and placed in a  $75 \pm 0.5^\circ$  bath. Ten minutes was allowed for temperature equilibration; then the black cloth was removed and the tube was ir-

radiated with a 200-watt incandescent lamp from a distance of 10 cm. for 24 hr. The tube was frozen with liquid nitrogen, then broken open in a vacuum line system under a pressure of  $10^{-6}$  mm. The reaction products were allowed to warm up to room temperature and the vapors were allowed to expand into a Toepler pump after passing through an efficient spiral trap maintained at  $-20^\circ$ . The contents of the Toepler pump were pushed into a U-tube equipped with stopcocks and the contents of the trap were refrozen into the remaining reaction mixture with liquid nitrogen. This distillation was repeated ten times; then only a trace of methyl chloride could be detected in the distillation residue by g.l.c. The contents of the U-tube were chromatographed on a 2-m. dinonyl phthalate column and the methyl chloride was collected and analyzed by mass spectrometry.

**Treatment of Mass Spectrometric Data.**—The machine was a Consolidated-Nier Isotope Ratio, Model 21-201, with a Gainsville-Philip variable slit leak; an ionizing voltage of about 150 v. and an accelerating voltage of about 900 v. were used. The relative amounts of methyl and methyl- $d_3$  chloride were determined from the 52 and 55 peaks. Corrections for the presence of 1.3% of methyl- $d_2$  chloride were made as follows: The 55 peak was assumed to be due entirely to  $CD_2Cl^{37}$ , an approximation good to high degree (see Table I). The amount of  $CD_2HCl^{37}$  is equal to 1.3% of the 55 peak; the amount of  $CD_2HCl^{36}$  is three times that value and it will contribute to the 52 peak. Therefore, 3.9% of the value of 55 peak was subtracted from the 52. This correction was applied to the relative sensitivity determinations as well. A further subtraction was made from the 52 peak for the amount of natural methyl chloride formed from hypochlorite molecules containing  $-CD_2H$ . This correction amounts to 1.6% of the 55 peak ( $1.3\% \times$  isotope effect in  $-CD_2H$  group). Reproducibility of the ratios obtained in this fashion was good,  $\pm 1\%$ .

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[CONTRIBUTION FROM THE PROCTER & GAMBLE CO., MIAMI VALLEY LABORATORIES, CINCINNATI 39, OHIO]

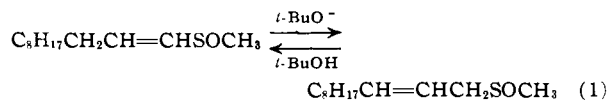
## The Effect of Methylmercapto, Methylsulfinyl, and Methylsulfonyl Groups on the Equilibrium in Three-Carbon Prototropic Systems

By D. E. O'CONNOR AND W. I. LYNES

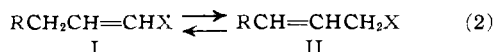
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The positions of base-catalyzed equilibrium between the  $\alpha,\beta$ - and  $\beta,\gamma$ -unsaturated isomers of alkenyl methyl sulfides, sulfoxides, and sulfones (eq. 2, X =  $-SCH_3$ ,  $-SOCH_3$ , and  $-SO_2CH_3$ ) have been determined. In the compounds containing an alkyl group attached to the  $\gamma$ -carbon atom, the ratios of  $\beta,\gamma$ - to  $\alpha,\beta$ -unsaturated isomers are: in sulfides (X =  $-SCH_3$ ), 34:66; in sulfoxides (X =  $-SOCH_3$ ), 96:4; in sulfones (X =  $-SO_2CH_3$ ), >99:1. In the allyl-propenyl equilibria the ratios of  $\beta,\gamma$ - to  $\alpha,\beta$ - are: in sulfides, <1:99; in sulfoxides, 20:80; in sulfones, 44:56. The great predominance of  $\beta,\gamma$ -isomers in the alkenyl methyl sulfoxides and sulfones is convincing evidence that ground-state d-orbital resonance contributes little or nothing to the stability of the  $\alpha,\beta$ -double bond. The data are rationalized on the basis that an inductive withdrawal of electrons destabilizes a double bond. Comparison of the case where R = alkyl with that where R = H in eq. 2 indicates that the stabilizing effect of the alkyl group is 2.8 kcal.

In an earlier communication,<sup>1</sup> we reported that the  $\beta,\gamma$ -unsaturated isomer is greatly favored over the  $\alpha,\beta$ -unsaturated isomer at equilibrium in the base-catalyzed isomerization of certain alkenyl methyl sulfoxides (eq. 1). Because this was the first case in which the  $\beta,\gamma$ -isomer was found to be favored in an open-chain sys-



tem, we wished to study the more general system (eq. 2) in which R is hydrogen or alkyl and X represents



(1) D. E. O'Connor and W. I. Lyness, *J. Am. Chem. Soc.*, **85**, 3044 (1963).

methylmercapto, methylsulfinyl, and methylsulfonyl groups. The effect of these groupings on the equilibrium is reported herewith.

Linstead and Kon and their co-workers have made a thorough investigation of the effect of certain other substituent groups, X, in the prototropic system depicted in eq. 2. In all such systems which they studied, I is more stable than II.

In esters (X =  $-CO_2R$ ) the ratio of I:II at equilibrium is approximately 92:8<sup>2</sup>; in carboxylic acids (X =  $-CO_2H$ ) or their salts (X =  $-CO_2^-$ ) the ratio is 68-75:32-25<sup>3,4</sup>; in nitriles (X =  $-CN$ ) the ratio is

(2) G. A. R. Kon, R. P. Linstead, and G. W. G. MacLennan, *J. Chem. Soc.*, 2452, 2454 (1932).

(3) A. A. Goldberg and R. P. Linstead, *ibid.*, 2343 (1928).

(4) R. P. Linstead and E. G. Noble, *ibid.*, 614 (1934).