was refluxed with 50% hydrochloric acid for 4 hours. The reaction mixture was worked up in the usual manner for isolation of an acid. A solid acid (1.8 g.) which crystallized in flat prisms was obtained, m.p. 83°. The infrared spectrum exhibited bands at 1690 and 1610 cm.$^{-1}$.

*Anal.* Calcd. for $C_5H_5Cl_3O_2$: C, 29.48; H, 2.46; Cl, 52.3; neut. equiv., 203.5. Found: C, 29.53; H, 2.53; Cl, 52.29; neut. equiv., 202.

**5,5-Dichloro-2,4-pentadienonitrile.**—3-Bromo-5,5,5-trichloropentanonitrile (27 g.) was heated in an oil-bath at 180° for 2 hours until hydrogen halide gases ceased to evolve. The brownish material was extracted with ether, the extract washed with dilute aqueous sodium hydroxide and dried over anhydrous sodium sulfate. Upon evaporating the ether and distilling the residual oil under reduced pressure, 11.8 g. of material was obtained as colorless oil, b.p. 41–42° (0.2 mm.); cooling at 0°, the substance crystallized in long prismatic crystals, m.p. 16°, $n^{23}D$ 1.5590. The ultraviolet spectrum showed a maximum absorption at 268 m$\mu$, $\Sigma_{max}$ 23300.

*Anal.* Calcd. for $C_5H_3Cl_2N$: C, 40.54; H, 2.02; Cl, 47.97; N, 9.45. Found: C, 40.43; H, 2.12; Cl, 48.04; N, 9.49.

**5,5-Dichloro-2,4-pentadienoic Acid.**—5,5-Dichloro-2,4-pentadienonitrile (3 g.) was refluxed with 50% hydrochloric acid (10 ml.) for 4 hours. The reaction mixture was allowed to cool, diluted with water and extracted with ether. The ether extract was dried over anhydrous sodium sulfate and evaporated. Long colorless needles (2.29 g.) were obtained from petroleum ether, m.p. 128°. The ultraviolet spectrum of the substance showed a maximum absorption at 268 m$\mu$, $\epsilon_{max}$ 25000.

*Anal.* Calcd. for $C_5H_4Cl_2O_2$: C, 35.92; H, 2.38; Cl, 42.51; neut. equiv., 167. Found: C, 36.01; H, 2.40; Cl, 42.64; neut. equiv., 167.9.

**Identification of the Products from the Reaction of 1,2-Dibromoethene with Bromotrichloromethane.**—The fraction b.p. 75° (25 mm.), $n^{27}D$ 1.5350 (of Table I) gave the analysis for 3-bromo-1,1,1-trichloropropene. The infrared spectrum exhibited bands at 3040 and 1740 cm.$^{-1}$. The structure was confirmed by ozonolysis. Decomposition of the ozonide with water and treatment of the resulting solution with 2,4-dinitrophenylhydrazine yielded a hydrazone which identified chloral. The infrared spectrum of the fraction b.p. 51° (3 mm.) was identical with that of an authentic sample of *sym*-tetrabromoethane.

Ann Arbor, Michigan

[A Joint Contribution from Oak Ridge National Laboratory, and The Physical Chemistry Laboratory, Oxford University]

# Studies Involving Isotopically Labelled Formic Acid and its Derivatives.[1] II. Relation of the Absolute Reaction Rates to the Magnitudes of the Isotope Effects in the Oxidation of Formic-C$^{13}$ Acid by Halogen Atoms

By Gus A. Ropp,[2a] C. J. Danby[2b] and D. A. Dominey[2c]

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For two reactions of formic-C$^{13}$ acid in which the rate steps involve extraction of hydrogen by halogen atoms, the rate isotope effects, $k_{12}/k_{13}$, have been carefully evaluated by methods involving mass spectrometric analysis of carbon-13 dioxide. The difference between the measured values of $k_{12}/k_{13}$ for the two reactions has been found to be in the direction that the slower reaction shows the greater degree of isotope fractionation. This principle which has also been noted in earlier studies is discussed in terms of the possible residual carbon-to-hydrogen bonding to be expected in the activated states for the two reactions.

## A. Introduction

The reported studies of isotope effects in organic reactions now number in the hundreds. Even the reviews and summaries are so numerous that general references to them here would be more confusing than enlightening. However, most of the research in this field is intended to (a) elucidate a reaction mechanism by comparing qualitatively or semi-quantitatively a measured isotope fractionation ratio with the ratio predicted from a possible mechanism of the reaction, or (b) explore the validity of some aspects of reaction rate theory by comparing—usually quantitatively—measured isotope fractionation factors with those which reaction rate theory would predict for a reaction whose rate step is understood. For studies of type (a), a mere qualitative reply as to whether isotope fractionation *does* or *does not* occur in a given instance is often sufficient to give the desired information about the reaction mechanism. It is in investigations of type (b), where quantitative correlation of experimental and theoretical values of isotope fractionation factors is usually sought, that the greatest difficulties arise. Granted that excellent work[3] has been done in developing from absolute reaction rate theory approximate expressions from which theoretical values of the isotope effect can, in principle, be calculated from spectroscopic data, the fact remains that the application of these expressions has been usually a matter of guesswork for all except the very simplest of reacting systems. Even on the experimental side many difficulties[4] arise and undoubtedly some questionable experimentally measured isotope fractionation factors have been reported.

It is believed that much useful information from experiments of type (b) might be obtained and several of the difficulties referred to above might be cancelled out by making comparative studies of the fractionation factors for a series of reactions all employing the same labeled reactant, formic acid. This molecule can be specifically labeled at either the carbon or oxygen atoms or in either position of the hydrogen atoms, and the various types of isotope effects might be correlated either within a

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[1] An initial study of isotope fractionation in a formic acid reaction was reported by Gus A. Ropp, A. J. Weinberger and O. K. Neville, This Journal, **73**, 5573 (1951).

[2] (a) Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.; (b) Physical Chemistry Laboratory, Oxford University, Oxford, England; (c) Balliol College, Oxford University, Oxford, England.

[3] J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949); Henry Eyring and F. W. Cagle, Jr., *J. Phys. Chem.*, **56**, 65 (1952).

[4] Gus A. Ropp, *J. Chem. Ed.*, **34**, 60 (1957).

given reaction or among different reactions. The formic acid molecule also has the advantage of having been rather thoroughly studied spectroscopically so that many of the data needed in estimation of the limiting theoretical values of the various intermolecular isotope effects are available. Furthermore, many formic acid reactions should be eminently well-adapted to precise isotope fractionation studies; this should be true particularly of those producing carbon dioxide as several such reactions can be carried out quantitatively or caused to go to any desired stage of completion. Further, carbon dioxide, which is readily isolated pure, is well suited as a product for isotopic analysis in cases of either carbon-13, carbon-14 or oxygen-18 labeling. In cases of carbon-13 fractionation studies, formic acid as a reactant has an additional advantage of being a monocarbon compound, a fact which simplifies the mass spectrometric analysis of the reacting material and the calculation of isotope fractionation factors.

Labeled formic acid molecules also have other advantages in isotope fractionation studies. They can be used in either gas or liquid phase reactions. The relatively low molecular weight should point up the influence of molecular weight on the degree of isotope fractionation which might be overlooked in studies of reactions of heavier molecules. Since reactions of formic acid which proceed by widely different types of mechanisms are known, the effect of mechanism type on the degree of isotope fractionation might be included in studies of the series of formic acid reactions being proposed.

Finally, the fact that the formic acid molecule contains a carboxyl group should usually facilitate separation of the starting material from the reaction product or products formed during the partial reaction studies which play an essential part in the precise evaluation of carbon and oxygen isotope effect ratios.

With the above ideas in mind a number of reactions of labeled formic acid or its immediate derivatives are being considered which might lead to worthwhile correlations of the relative or absolute isotope fractionation factors with values estimated[3] from reaction rate theory. In the present paper two gas-phase oxidations of carbon-13 labeled formic acid having widely different absolute reaction rates were compared as to the degree of carbon-13 fractionation occurring in each. The purpose of this study was to investigate the effect of the absolute rate of reaction on the magnitude of the isotope effect.

## B. Method in the Present Study

Two photochemical reactions of formic acid, a rather rapid chlorination[5] and an analogous but

$$\underset{\substack{\text{(monomer}\\ \text{and dimer)}}}{Cl_2 + HC^{13}OOH} \xrightarrow[\substack{\text{light}\\ 20°}]{\text{visible}} 2HCl + C^{13}O_2$$

much less rapid bromination, were studied in the usual manner employing the 1% of natural carbon-13 present in the formic acid, and the ratios, $k_{12}/k_{13}$, obtained in the two reactions were compared.

$$\underset{\substack{\text{(monomer}\\ \text{and dimer)}}}{Br_2 + HC^{13}OOH} \xrightarrow[\substack{\text{light}\\ 45°}]{\text{visible}} 2HBr + C^{13}O_2$$

These reactions were found to be ideally suited in most respects for very precise determination of the isotope effects. Both reactions were completely quantitative and the isotope effects in each could therefore be determined in two ways. First, the carbon-13 concentration in the first 10 to 25% of carbon dioxide produced was compared with the carbon-13 content of the carbon dioxide from 100% reaction. Secondly, the carbon-13 concentration of the formic acid remaining after 80 to 90% reaction was compared with the original formic acid used. The latter method is a particularly sensitive means of evaluation of $k_{12}/k_{13}$ because the difference between specific activities of unreacted starting material and products becomes large at high percentages of reaction.

The reaction is somewhat complicated experimentally by the fact that monomeric and dimeric formic acid molecules react simultaneously at about the same rate.[5] However, there is every reason to suppose that the isotope effect ratios, $k_{12}/k_{13}$, should have the same value for reactions of monomer and dimer since the controlling feature of the reaction appears to be the cleavage of the carbon-to-hydrogen bond in each case.

## C. Experimental

**Formic Acid.**—The formic acid used was reagent 99% acid dried with anhydrous copper sulfate, which was found to contain 99.1% formic acid by actual titration. The vapor was stored in a large glass bulb for ready introduction into the vacuum line in which the reaction was run. Since some decomposition might occur to form carbon monoxide and water, the vapor was frozen with liquid air in a nipple on the bulb and any non-condensable gas was evacuated with a pump just before each run.

**Halogens.**—Pure dry chlorine and bromine were prepared and stored in bulbs as vapors. Before each run the halogen used was frozen down and non-condensable gas was evacuated in the same manner as described with the formic acid.

**Reaction System.**—Reactions were carried out in a 5-liter bulb connected to the vacuum line and to a mercury manometer, the surface of which was protected from reaction with halogens by a coating of fluorocarbon oil. The 5-liter bulb was kept in a glass battery jar filled with water thermostated at the desired temperature. Illumination was provided by a 750 watt lamp outside the battery jar at a distance of 8 cm. from the reaction bulb.

**Product Collection and Isotopic Analysis Systems.**—A 10-ml. trap in the line leading from the 5-liter reaction bulb to the vacuum line provided a point in which unreacted formic acid could be frozen at Dry Ice temperature after each run. Carbon dioxide and the hydrogen halide produced could then be frozen out with liquid air in a larger trap attached to the vacuum line. From this trap the carbon dioxide and hydrogen halide were expanded into a 1-liter bulb containing saturated barium hydroxide. Precipitated barium carbonate samples were collected on a filter, washed thoroughly with water, dried at 110–120°, and weighed. Small samples of barium carbonate were decomposed with degassed C.P. sulfuric acid and the isotopic analysis carried out with a Metropolitan–Vickers mass spectrometer, type M.S. 2. All samples were compared, using a double inlet arrangement, with standard samples of carbon dioxide produced from the 100% reaction. With each sample the appropriate peaks were traced repeatedly on the automatic recorder. All samples to be compared with one another were analyzed on one day to reduce errors due to instrument drifts. Tables I and II present the analyses reduced to percentage carbon-13 and the derived rate constant ratios with calculated means and their confidence intervals.

**Procedure Followed in Chlorine Reactions.**—In a typical reaction with chlorine with the bath at 20° the bulb was

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[5] H. L. West and G. K. Rollefson, THIS JOURNAL, **58**, 2140 (1936).

TABLE I

ISOTOPE EFFECT IN PHOTOCHEMICAL CHLORINATION OF FORMIC ACID AT 20°

| Reaction, % | Carbon-13, %[a] | Bracketing 100% Rx samples | | $k_{12}/k_{13}$ |
|---|---|---|---|---|
| 18 | 1.1325<br>1.1322 | 1.1413 | 1.1415 | 1.008 |
| 12 | 1.1354<br>1.1314 | 1.1414 | .... | 1.007 |
| 82 | 1.1400 | 1.1414 | .... | 1.004 |
| Last 18 | 1.1566<br>1.1605 | 1.1380 | .... | 1.010 |
| Last 16 | 1.1639<br>1.1608<br>1.1579 | 1.1413 | .... | 1.009 |
| Mean and 95% conf. interval | | | | 1.008 ± 0.002 |

[a] Duplicates represent duplicate fillings with same $CO_2$ sample. For each gas filling 6 or 8 peak height ratios (in mm.) were averaged.

TABLE II

ISOTOPE EFFECT IN PHOTOCHEMICAL BROMINATION OF FORMIC ACID AT 45°

| Reaction, % | Carbon-13, %[a] | Bracketing 100% Rx samples | | $k_{12}/k_{13}$ |
|---|---|---|---|---|
| 17 | 1.1070 | 1.1334 | 1.1336 | 1.027 |
| | 1.1030 | 1.1308 | | 1.027 |
| 25 | 1.1008 | 1.1298 | 1.1302 | 1.030 |
| | 1.1016 | 1.1308 | | 1.030 |
| 85 | 1.1208 | 1.1308 | 1.1302 | 1.027 |
| | 1.1206 | 1.1336 | 1.1353 | 1.035 |
| Last 15 | 1.1918 | 1.1308 | 1.1302 | 1.027 |
| | 1.1893 | 1.1298 | 1.1353 | 1.027 |
| Mean and 95% conf. interval | | | | 1.029 ± 0.002 |

[a] Duplicates represent duplicate fillings with same $CO_2$ sample. For each gas filling 6 or 8 peak height ratios (in mm.) were averaged.

charged with 19 mm. formic acid and 4.2 mm. chlorine in the dark. This was sufficient chlorine for 12.5% reaction of the formic acid taking into account the fact that formic acid vapor consists of 78% dimer under these initial conditions.[6] The light was turned on and the calculated pressure change, 8 mm., was found to occur in 25 minutes. Using the product separation procedure described above, 249 mg. of dry barium carbonate was recovered. The theoretical weight based on the pressure of chlorine used was 240 mg.

To obtain a sample of barium carbonate corresponding to 100% reaction of the formic acid used, a larger sample of formic acid was treated with excess chlorine for a long period of time to ensure complete reaction of the acid.

In another run the bulb was charged with 22 mm. of formic acid and 32.5 mm. of chlorine which was calculated to react with 83% of the formic acid. After approximately 50 minutes the pressure ceased to change. The weight of barium carbonate recovered dry was 1840 mg. The percentage reaction based on this weight was 81%. The residual unreacted formic acid was then allowed to expand into the evacuated bulb and was chlorinated using excess chlorine. The recovered dried barium carbonate from this portion of the reaction weighed 436 mg. as compared with 432 mg. calculated for the last 19% of reaction.

**Procedure Followed in Bromine Reactions.**—The procedure for the bromine reaction at 45° was analogous to that for the chlorine reaction at 20°. Even at 45°, 16 to 17% reaction of the formic acid required about ten hours so that the rate constants for the bromine and chlorine reactions must differ by a factor of fifty to one hundred.

Brominations carried to 80% reaction or further required many hours reaction time, and to speed up the study the residual formic acid was oxidized quantitatively in hot aqueous solution with bromine.

**D. Correction of Experimental Isotope Effect Ratios to Eliminate the Effect of the Molecular Mass of the Formic Acid on the Collision Frequency.**—It is desirable to eliminate the effect of the isotope on the collision frequency in each reaction in order that the net activation energy isotope effects can then be compared. These collisional isotope effects were calculated as shown in Tables III and IV and the calculation of the net activation energy isotope effects is shown in Table V.

TABLE III

CALCULATION OF COLLISION FREQUENCY ISOTOPE EFFECT IN THE REACTION OF Cl· WITH FORMIC ACID VAPOR

| | | |
|---|---|---|
| $HC^{12}OOH$ *vs.* $HC^{13}OOH$ | $\sqrt{\frac{46 + 35.5}{46 \times 35.5} \Big/ \frac{47 + 35.5}{47 \times 35.5}}$ | 1.0047 |
| $(HC^{12}OOH)_2$ *vs.* $(HC^{12}OOH \cdot HC^{13}OOH)$ | $\sqrt{\frac{92 + 35.5}{92 \times 35.5} \Big/ \frac{93 + 35.5}{93 \times 35.5}}$ | 1.0015 |
| | Mean weighted for: (a) 78% dimer and (b) monomer *vs.* dimer = 1.13 | 1.0022 |

TABLE IV

CALCULATION OF COLLISION FREQUENCY ISOTOPE EFFECT IN THE REACTION OF Br· WITH FORMIC ACID VAPOR

| | | |
|---|---|---|
| $HC^{12}OOH$ *vs.* $HC^{13}OOH$ | $\sqrt{\frac{46 + 80}{46 \times 80} \Big/ \frac{47 + 80}{47 \times 80}}$ | 1.0068 |
| $(HC^{12}OOH)_2$ *vs.* $(HC^{12}OOH \cdot HC^{13}OOH)$ | $\sqrt{\frac{92 + 80}{92 \times 80} \Big/ \frac{93 + 80}{93 \times 80}}$ | 1.0025 |
| | Mean weighted for (a) 43% dimer and (b) monomer *vs.* dimer = 1.21 | 1.0051 |

TABLE V

ESTIMATES OF THE NET (ACTIVATION ENERGY) ISOTOPE EFFECTS IN PHOTOCHEMICAL HALOGENATION OF FORMIC ACID

| Reaction | $k_{12}/k_{13}$ |
|---|---|
| $Cl\cdot + HR \longrightarrow HCl + R\cdot$ | 1.008/1.0022 = 1.006 |
| $Br\cdot + HR \longrightarrow HBr + R\cdot$ | 1.029/1.0051 = 1.023 |

**E. Calculation of the Maximum Theoretical Value of the Carbon-13 Rate Isotope Effect in Cleavage of a Carbon-to-Hydrogen Bond.**—Since the important frequencies about the carbon-to-hydrogen linkage in formic acid monomer have been established,[7] estimation of the maximum expected carbon-13 isotope effect by the method outlined by Bigeleisen[3] and Eyring[3] is not difficult if certain assumptions are allowed. The C–H frequencies in the normal molecule were taken to be 2943 cm.$^{-1}$ stretching, an in-plane swaying of 1346 cm.$^{-1}$ and an out-of-plane swaying of 1033 cm.$^{-1}$. To arrive at a maximum isotope effect these frequencies are assumed to vanish in the activated complex. The carbon-oxygen bond frequencies are assumed to remain unaltered in proceeding from the normal molecule to the activated complex. Applying the approximation based on the unimolecular reaction theory of Slater[8] that the isotope effect on the frequency in the reaction coördinate may be estimated using the ratio of reduced masses of atoms joined directly by the bond undergoing cleavage, the calculated values of $k_{12}/k_{13}$ are 1.032 at 20° and 1.029 at 45°. It should be pointed out in passing that the present research supports earlier work on the general magnitude of the isotope effect to be expected in carbon-to-hydrogen bond cleavage.[9] In that work cleavage of a carbon-14-to-hydrogen bond was found experimentally to show a carbon-14 rate isotope effect such that $k_{12}/k_{14}$ was approximately 1.035 at 38°. Carbon-14 isotope effects can be expected to have values about twice the magnitude of carbon-13 effects in the same reaction. Therefore, the earlier reaction[9] if studied with carbon-13 could be expected to show a $k_{12}/k_{13}$ ratio of

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(6) A. S. Coolidge, THIS JOURNAL, **50**, 2166 (1928).

(7) J. K. Wilmshurst, *J. Chem. Phys.*, **25**, 478 (1956).

(8) N. B. Slater, *Proc. Roy. Soc.* (*London*), **A194**, 112 (1948).

(9) Gus A. Ropp and Ernest M. Hodnett, *J. Chem. Phys.*, **25**, 587 (1956).

perhaps 1.015 to 1.02 at 38°. This checks reasonably well with the net isotope effect, $k_{12}/k_{13} = 1.023$, found in the present bromination of formic acid at 45°, though not so well with the chlorination isotope effect reported here. Arguments set forth below may explain the low isotope fractionation factor found in the chlorination of formic acid.

## F. Discussion of the Results

Two series of carbon-14 isotope effects were studied earlier in attempts to evaluate the effect of the absolute reaction rate on $k_{12}/k_{14}$, the ratio of the rate constants.[10] In these studies the faster reactions were found to result in $k_{12}/k_{14}$ values which were closer to unity, meaning the least degree of isotope fractionation. However, since the labeled molecules differed by variations in the character of the nuclear substituents in those series, the trend in the values of $k_{12}/k_{14}$ could not necessarily be attributed entirely to changes in the absolute reaction rates within the series. The present study does not suffer from such limitations because the labeled molecule, formic-$C^{13}$ acid, was the same in the two reactions compared.

Other such series which employed hydrogen isotope effects have been discussed by Wiberg.[11] These, however, appear to be complicated by both the occurrence of *intramolecular* isotope effects and experimental difficulties due to the ease of hydrogen exchange, and the interpretation is more difficult although it appears that the least reactive radicals give the greatest hydrogen isotope effects during abstraction of hydrogen from organic molecules.

As Table V reveals the reaction of chlorine with formic-$C^{13}$ acid at 20° gives a much lower net isotope effect than that with the slower reaction of bromine at 45°. Although the measured carbon-13 isotope effects are small, the difference between the two is well outside of that which can be attributed to experimental error as examination of Tables I and II reveals. Since it is well established that lower isotope effects are to be expected at higher temperatures, the difference between the isotope effects for the two reactions would be still greater if they were run at the same temperature.

Many experimentalists tend to feel intuitively that greatest product selectivity should generally be expected in slow reactions. In the case of organic chemists this feeling might be traced back to the knowledge that side reactions in syntheses generally are less prevalent at lower temperatures where the main reaction is slowest.

General consideration of the mechanism of reaction of halogen atoms with formic acid[5] leads to the conclusion that, from the standpoint of carbon or hydrogen isotope effects, the only important step is the hydrogen extraction for which an activated state may be of the type shown in brackets

$$X\cdot + HCOOH \longrightarrow [X{-}{-}{-}H{-}{-}{-}COOH] \longrightarrow HX + \cdot COOH \quad \text{(i)}$$

Thus the reaction is analogous in its rate step to the photochemical reaction of halogens with hydrogen

$$X\cdot + H_2 \longrightarrow [X{-}{-}{-}H{-}{-}{-}H] \longrightarrow HX + H\cdot \quad \text{(ii)}$$

The rate step is also like that in the reaction of chlorine atoms with certain hydrocarbons

$$Cl\cdot + HR \longrightarrow [Cl{-}{-}{-}H{-}{-}{-}R] \longrightarrow HCl + R\cdot \quad \text{(iii)}$$

for which the activated state has recently been discussed[12] and is believed to have carbon-to-hydrogen and chlorine-to-hydrogen bond lengths only slightly stretched as compared with the corresponding bonds in the normal hydrocarbon and in hydrogen chloride.

Semi-quantitative discussion of the effect of the absolute reaction rate on the carbon-13 isotope effect in the two photochemical halogenations of formic acid is best handled in terms of absolute reaction rate theory as Wiberg[11] has done for certain hydrogen isotope effects. In Fig. 1 the isotopic zero-point energy levels for vibration of the carbon-to-hydrogen bond in the normal molecule are shown at C and the corresponding zero-point energy levels of the activated state are shown at C*. Farkas and Farkas[13] and Bell[14] have supplied evidence for and discussed the zero-point energy in the activated state of certain reactions. From Fig. 1 it is apparent that the difference between the activation energies, $E_{13} - E_{12}$, for the rate step in the reactions of two isotopic species is greatest in reactions in which the isotopic spread of levels in the activated complex is smallest. Thus if two reactions of formic-$C^{13}$ acid are compared as to their values of $k_{12}/k_{13}$, the spread of the isotopic levels in the normal molecule should be the same in both reactions, if the experimental conditions are alike in the pair of reactions. Then that reaction which has the weakest residual bonding of the carbon atom in the activated state will be expected to show a value of $k_{12}/k_{13}$ with the greatest deviation from unity. Therefore in order to decide whether the chlorine reaction or the bromine reaction should be expected to show the greater value of $k_{12}/k_{13}$, it is necessary to decide which reaction would be expected to proceed through a complex with the greater residual carbon-to-hydrogen bonding. As already has been mentioned, it appears that the bonding in the activated state in the analogous reaction (iii) of chlorine with hydrocarbons[12] is not greatly different

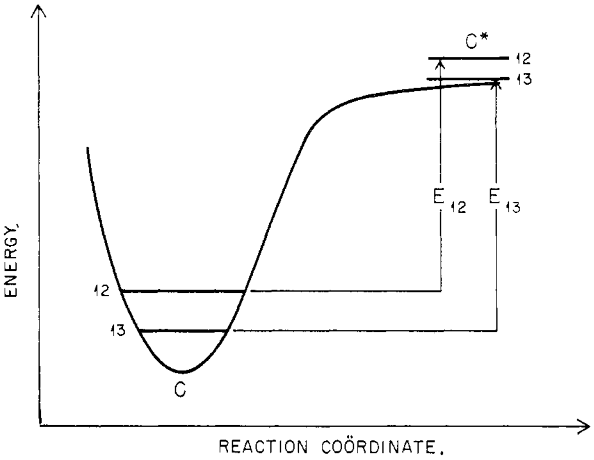

Fig. 1.—Rate isotope effect of residual bond strength in the activated state.

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[10] Gus A. Ropp and V. F. Raaen, *J. Chem. Phys.*, **22**, 1223 (1954).

[11] K. Wiberg, *Chem. Revs.*, **51**, 730 (1955).

[12] J. H. Knox and A. F. Trotman-Dickenson, *J. Chem. Phys.*, **60**, 1367 (1956).

[13] A. Farkas and L. Farkas, *Proc. Roy. Soc.* (*London*), **152A**, 124, 152 (1935).

[14] R. P. Bell, "Acid–Base Catalysis," Oxford Univ. Press, Oxford, England, 1941, p. 159.

from the bonding in the normal reactants. Therefore this reaction and the similar chlorination of formic acid could both be expected to show much smaller carbon-13 isotope effects than those theoretically calculated assuming complete loss of the carbon-to-hydrogen bond in proceeding to the activated state. This was borne out in the chlorination of formic-$C^{13}$ acid at 20° since the theoretically calculated maximum value of $k_{12}/k_{13}$ was 1.032 and the net experimental value was only 1.006. In the case of the bromination reaction at 45° the net experimental value of $k_{12}/k_{13}$, 1.023, was much closer to the theoretically calculated value, 1.029, as might be expected if the activated state for the bromine reaction retained considerably less residual carbon-to-hydrogen bond strength than the activated state for the chlorine reaction. The much slower bromine reaction having the higher activation energy might be expected to retain less of its carbon–hydrogen bond strength at the higher energy level of its activated state. In other words it appears that the carbon–hydrogen bond must be stretched more before cleavage can be effected by a bromine atom than before the corresponding cleavage can occur under the influence of a more active chlorine atom.

Assuming this to be the correct explanation of the difference in degree of isotope fractionation with the two types of halogen atoms, it is interesting to speculate upon what might be the relative hydrogen rate isotope effects due to deuterium or tritium labeling in the same pair of reactions; that is

$$\mathrm{Cl\cdot + DCOOH \longrightarrow [Cl{-}{-}{-}D{-}{-}{-}COOH] \longrightarrow DCl + \cdot COOH} \quad (j)$$

and

$$\mathrm{Br\cdot + DCOOH \longrightarrow [Br{-}{-}{-}D{-}{-}{-}COOH] \longrightarrow DBr + \cdot COOH} \quad (jj)$$

It would seem that $(k_H/k_D)_{Cl}$ might bear about the same relation to $(k_H/k_D)_{Br}$ as $(k_{12}/k_{13})_{Cl}$ was found to bear to $(k_{12}/k_{13})_{Br}$. Whether or not this would be found to be the case might depend upon the importance of the X—H bond in the activated state. It is planned to study these deuterium (and/or tritium) isotope effects and to compare them with the corresponding carbon-13 (and possibly the carbon-14) effects. Although there is considerable uncertainty in calculating theoretical values of either carbon or hydrogen isotope effects, it may well be that the ratio of the carbon isotope effect to the hydrogen isotope effect would be easier to predict than either effect individually. If so, it may be of value to compare ratios such as

$$\left[\frac{k_H/k_D}{k_{12}/k_{13}}\right]_{Cl} \quad \text{and} \quad \left[\frac{k_H/k_D}{k_{12}/k_{13}}\right]_{Br}$$

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# An Oxygen-18 Tracer Study of the Rearrangements of 2-Phenyl-1-propyl *p*-Bromobenzenesulfonate and 2-*p*-Methoxyphenyl-1-propyl *p*-Toluenesulfonate[1]

BY DONALD B. DENNEY AND BERNARD GOLDSTEIN

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2-Phenyl-1-propyl *p*-bromobenzenesulfonate, which was specifically labeled in the ether oxygen of the ester group with oxygen-18, was allowed to rearrange in acetic acid to give 1-phenyl-2-propyl *p*-bromobenzenesulfonate. The ester was reduced with sodium in ammonia to afford benzylmethylcarbinol. The oxygen-18 content of this molecule showed that during the rearrangement partial equilibration of the label took place. In a similar manner 2-*p*-methoxyphenyl-1-propyl *p*-toluenesulfonate was rearranged to give 1-*p*-methoxyphenyl-2-propyl *p*-toluenesulfonate. The oxygen-18 content of the alcohol, obtained by the reductive cleavage of the *p*-toluenesulfonate, showed that during this transformation the three oxygens of the *p*-toluenesulfonate moiety became equivalent.

The mechanism of solvolytic reactions has received a great deal of attention. The reviews[2] of this subject are numerous and cover it in great detail. Recently Winstein[3] and his co-workers have investigated a considerable number of these reactions with a view toward elucidating the role of ion pairs in these systems. In the course of their investigations they found that 2-phenyl-1-propyl *p*-bromobenzenesulfonate (VII) rearranged in acetic acid to give 1-phenyl-2-propyl *p*-bromobenzenesulfonate (IX).[4] They observed that the addition of *p*-bromobenzenesulfonate ion to the reaction mixture did not cause a common ion rate suppression, but rather only a normal salt effect was observed. On the basis of these results and other data, they suggested that the rearrangement of VII to IX proceeded through an ion pair, which was held together by coulombic attraction and also possibly by some covalent bonding. They have called ion pairs of this sort "internal" or "intimate."

They have also investigated the solvolysis of 2-

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[1] Presented at the Sixth Conference on Reaction Mechanisms, Swarthmore College, Sept. 12–15, 1956.

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