

The Primary Carbon Isotope Effect on the Ionization of Triphenylmethyl Chloride. Experimental Determination, Theoretical Justification, and Implications for Carbon Isotope Effects on Nucleophilic Substitution at Saturated Carbon¹⁻³

A. J. Kresge,⁴ N. N. Lichtin,⁵ K. N. Rao,⁵ and R. E. Weston, Jr.⁶

Contribution from the Departments of Chemistry of Boston University, Boston, Massachusetts, Brookhaven National Laboratory, Upton, New York, and the Illinois Institute of Technology, Chicago, Illinois.

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The carbon-13 isotope effect on the ionization of triphenylmethyl chloride to triphenylcarbonium ion has been determined by measuring the electrical conductivities of normal triphenylmethyl chloride and triphenylmethyl-1-¹³C chloride in liquid sulfur dioxide solution at 0°: $K_{12}/K_{13} = 0.9833 \pm 0.0032$. A theoretical analysis of this isotopic system shows that this unusual inverse isotope effect can be reproduced in a model system of abbreviated "molecules" which consist only of the isotopically substituted atom and the atoms bonded directly to it. This analysis also reveals that the cause of the inverse isotope effect in the real system must be much stronger carbon-phenyl bonds in triphenylcarbonium ion than in triphenylmethyl chloride; this bond strengthening is enough to offset the loss of a carbon-chlorine bond. An extension of this reasoning provides an explanation for the unusually small kinetic isotope effects which have been observed in SN1 substitution at carbon.

Introduction

The rate-determining step in nucleophilic substitution at saturated carbon by the SN1 mechanism consists of the breaking of a bond to carbon with no concomitant covalent bond formation. Since this is a pure bond-breaking process, it should show a large primary carbon isotope effect. However, quite the opposite has been observed experimentally. The hydrolysis of *t*-butyl chloride in aqueous dioxane at 25° has a carbon-14 isotope effect of 1.037 (k_{12}/k_{14}) and the solvolysis of α -phenylethyl bromide has carbon-13 isotope effects of 1.007 (k_{12}/k_{13}) in methanol at 25° and 1.006 (k_{12}/k_{13}) in ethanol at 45°.⁸ These are unusually small rate ratios for bond breaking at carbon. They are, moreover, significantly smaller than carbon isotope effects observed in SN2 substitution,⁹ which is a process in which bond formation accompanies bond

breaking and which might be expected, therefore, to show smaller isotope effects than SN1 substitution.

It has been suggested that these unexpectedly small isotope effects in SN1 substitution are the result of secondary changes in the nonreacting bonds to the carbon atom at which substitution is taking place.^{3,8} As reaction occurs, these bonds will be strengthened through conjugative interaction between the developing positive charge and neighboring phenyl or methyl groups. Such conjugation increases the bond order of these bonds, this increase in bonding offsets the decrease produced by breaking of the reacting bond, and this compensation serves to lower the isotope effect.

It is difficult to verify this explanation in the systems to which it pertains. The magnitude of kinetic isotope effects depends on mechanical properties of transition states as well as initial states. Since transition states cannot be observed directly, their translations, rotations, and vibrations cannot be determined with certainty. Isotope effects on equilibria, however, are more amenable to exact calculation. Here the two states involved are both stable, each can be observed directly, and their properties can, at least in principle if not always in practice, be determined completely. Kinetic processes are commonly interpreted in terms of equilibrium reactions between initial states and transition states, and this is, in fact, the treatment universally employed in theoretical discussions of isotope effects. Since, from this point of view, there is no fundamental difference between kinetic and equilibrium phenomena, information concerning the low magnitude of isotope effects on SN1 substitution might be obtained from examination of suitable equilibrium reactions.

The ionization of triphenylmethyl chloride in liquid sulfur dioxide is a reaction which quickly comes to equilibrium giving triphenylmethyl cation and chloride anion uncomplicated by secondary changes.¹⁰ This process is a good model for SN1 substitution at saturated carbon; indeed, it can be considered to be a limiting SN1 reaction, *i.e.*, a process completely devoid of SN2 character. We have, therefore, examined the carbon isotope effect on this equilibrium in an effort to gain insight into kinetic isotope effects on SN1 substitution.

Isotope effects can be measured by two general methods: direct determination of rate or equilibrium constants for normal and labeled species in separate experiments, and comparison of isotopic content of

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(2) Paper X in the series "Ionization and Dissociation Equilibria in Liquid Sulfur Dioxide."

(3) For a preliminary communication, see A. J. Kresge, N. N. Lichtin, and K. N. Rao, *J. Am. Chem. Soc.*, **85**, 1210 (1963).

(4) Department of Chemistry, Illinois Institute of Technology.

(5) Department of Chemistry, Boston University.

(6) Department of Chemistry, Brookhaven National Laboratory.

(7) M. L. Bender and G. J. Buist, *J. Am. Chem. Soc.*, **80**, 4304 (1958).

(8) J. B. Stothers and A. N. Bourns, *Can. J. Chem.*, **38**, 923 (1960).

(9) (a) M. L. Bender and D. F. Hoeg, *J. Am. Chem. Soc.*, **79**, 5649 (1957); (b) G. J. Buist and M. L. Bender, *ibid.*, **80**, 4308 (1958); K. R. Lynn and P. E. Yankwich, *ibid.*, **83**, 53, 790, 3220 (1961).

(10) N. N. Lichtin in "Progress in Physical Organic Chemistry," Vol. I, Interscience Publishers, New York, N. Y., 1963, pp. 87-100.

reactants and/or starting material in an experiment in which both species are allowed to react simultaneously. The second of these techniques, the competition method, is usually an order of magnitude more precise than the first, and since carbon isotope effects are seldom greater than 1.1, the competition method has been used exclusively for their measurement. This method requires separate isotopic analysis of starting materials and reactants (or starting material before reaction and near complete reaction) and so depends for its success on a clean separation of reactants and products. The equilibrium between triphenylmethyl chloride and triphenylmethyl cation, however, is a very mobile one, and products cannot be isolated without disturbing the system. Fortunately, the extent of ionization of triphenylmethyl chloride can be measured by a conductometric method which is capable of high precision,¹⁰ and the ratio of two ionization constants can be determined to $\pm 0.3\%$.¹¹ This approaches the precision obtainable with the competition method. Carbon-13 is now available at high enrichments, and an experiment in which equilibrium constants of normal triphenylmethyl chloride and triphenylmethyl-1-C¹³ are determined separately is feasible. The results of such an experiment are described below. We believe this to be the first instance of the determination of a carbon isotope effect by separate measurements of two rate or equilibrium constants.

Experimental

Benzoic- α -C¹³ Acid. The vacuum line method of carbonating Grignard reagents described by Murray and Williams¹² was employed. From 250 ml. of 0.22 *M* phenylmagnesium bromide in ethyl ether and 10.5 g. of barium carbonate-C¹³ (Atomic Energy Research Establishment, Harwell, England, 66.1 atom % carbon-13), 4.85 g. of benzoic- α -C¹³ acid was obtained (75% yield), m.p. 121.5–122.2°, 66.0 \pm 0.5 atom % of carbon-13 at the labeled position.¹³

Triphenylmethanol-1-C¹³. Benzoic- α -C¹³ acid (4.75 g.) was esterified with absolute ethanol (10 ml.) in benzene (30 ml.) with a sulfuric acid catalyst (5 drops). The mixture was heated under reflux and water was withdrawn by azeotropic distillation as it formed. When no more water separated, the reaction mixture was cooled, washed with water, dilute aqueous sodium bicarbonate, and water, and the resultant benzene solution was dried over Drierite. The benzene was removed by fractional distillation through an efficient column (10–15 plates), and the residue was used directly for reaction with phenylmagnesium bromide.

The ester, dissolved in 20 ml. of dry benzene, was added under a nitrogen atmosphere to 100 ml. of well-stirred 1.1 *M* phenylmagnesium bromide in ethyl ether at a rate just sufficient to maintain reflux. The reaction mixture was then heated under reflux for 2 hr., cooled, and decomposed with dilute aqueous sul-

furic acid. The ether layer was separated and washed with water, dilute aqueous sodium bicarbonate, and water. The solvent was removed in a nitrogen stream at steam bath temperature and the pasty residue subjected to steam distillation. The yellow solid, remaining after about 300 ml. of steam distillate had been collected, was collected, dried, and recrystallized from hexane to give 5.92 g. (60% yield) of white crystalline solid, m.p. 149–158°. This material was purified by repeated recrystallization alternately from methanol and from hexane. Three recrystallizations gave 3.50 g. of triphenylmethanol-1-C¹³, m.p. 162.2–163.0°, 65.1 \pm 0.4 atom % carbon-13 at the labeled position.¹³

Triphenylmethyl-1-C¹³ Chloride. A solution of triphenylmethanol-1-C¹³ (3.40 g.), acetyl chloride (2.3 g., J. T. Baker Chemical Co., Analyzed reagent), and sodium-dried benzene (1.1 ml.) was heated under reflux for 1 hr. while protected from atmospheric moisture. The resulting clear solution was cooled in an ice bath and 3.0 ml. of cold, dry pentane was added. The granular precipitate which formed was collected rapidly by suction filtration, washed with a small amount of cold pentane, and dried in a vacuum desiccator. The dried material weighed 2.40 g. (68% yield), m.p. 111–113°. This was purified by recrystallization from ethyl ether in an apparatus which allowed crystallization and suction filtration in a nitrogen atmosphere. Recrystallization was repeated until a substance with a sharp melting point of 113° was obtained. (Usually two to three recrystallizations were sufficient.) The purified substance contained 65.6 \pm 0.1 atom % of carbon-13 at the labeled position.¹³

Triphenylmethyl Chloride. Unlabeled material was prepared from normal barium carbonate (Mallinckrodt, analytical reagent) by a procedure identical with that described for the C¹³-labeled compound. Isotopic analysis confirmed normal abundance of carbon-13 (1.1 atom %).

Analysis of Solutes. Two different preparations (A and B) of each of the solutes, triphenylmethyl chloride and triphenylmethyl-1-C¹³ chloride, were used. Their equivalent weights were determined by dissolving aliquots in purified acetone, hydrolyzing with excess 0.1 *N* alkali, and determining the remaining base by acidimetric titration to a bromothymol blue end point. Standard deviations of replicate analyses were no greater than $\pm 0.1\%$. Triphenylmethyl chloride: preparation A (I), 278.5; preparation B (I, II, III), 278.7; theory, 278.8. Triphenylmethyl-1-C¹³ chloride: preparation A (I), 279.3; preparation B (II, III), 279.1; theory, 279.4. The Roman numerals following the letter designating a given preparation indicate the groups of conductance runs in which it was employed (see next section).

Conductance Measurements. All solutions of labeled and unlabeled triphenylmethyl chloride in sulfur dioxide were prepared on the vacuum line by procedures which have been described previously^{14–16} using redistilled and degassed Virginia Smelting Co. "Extra Dry" or Matheson "Anhydrous" sulfur dioxide. Conductances were measured with a bridge¹⁶ in three

(11) N. N. Lichtin, E. S. Lewis, E. Price, and R. R. Johnson, *J. Am. Chem. Soc.*, **81**, 4520 (1959).

(12) A. R. Murray and D. L. Williams, "Organic Synthesis with Isotopes," Interscience Publishers, Inc., New York, N. Y., 1958, part I, p. 86.

(13) Carbon-13 assay was performed by Dr. D. R. Christman of Brookhaven National Laboratory. Carbon dioxide resulting from complete combustion was subjected to mass spectrometric analysis, and isotopic content at the labeled position was calculated assuming all other carbons had the natural abundance of carbon-13 (1.1%).

(14) N. N. Lichtin and H. P. Leftin, *J. Phys. Chem.*, **60**, 160 (1956).

(15) N. N. Lichtin and P. D. Bartlett, *J. Am. Chem. Soc.*, **73**, 5537 (1951).

(16) N. N. Lichtin and H. Glazer, *ibid.*, **73**, 5537 (1951).

Table I. Mean Values for Individual Sets of Conductance Measurements

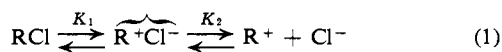
Set ^a	—Number of solutions—		—Dilution of the solutions, M^{-1} —		K_{12}/K_{13}^b	Std. dev. of mean
	$(C_6H_5)_3CCl$	$(C_6H_5)_3C^{13}Cl$	$(C_6H_5)_3CCl$	$(C_6H_5)_3C^{13}Cl$		
I	6	6	278.1 ± 1.5^c	277.2 ± 2.1^c	0.9876	0.0061
II	6	8	87.3 ± 4.1^c	85.5 ± 4.2^c	0.9866 ^d	0.0043
III	7	8	289.7 ± 0.5^c	291.3 ± 1.1^c	0.9901 ^d	0.0026
Grand mean:					0.9890	0.0021

^a See *Conductance Measurements* section of the text. ^b Experimental results *not* corrected to 100% carbon-13 at the labeled position. ^c Mean deviation. ^d Where two different carbon-13 data points were paired with the same carbon-12 value, the K_{12}/K_{13} ratio was given a statistical weight of 0.75.

different kinds of cells; these measurements are designated sets I, II, and III. Resistances were measured to at least ± 0.5 ohm which corresponds to a precision of $\pm 0.03\%$ or better. The measurements of set I were made in a single internal dilution cell which has already been described.¹¹ The measurements of sets II and III were made in cells of 5-ml. and 50-ml. capacity, respectively, which were otherwise similar to the electrode arm of the internal dilution cell used in set I except that no mixing bulb was provided. Mixing was accomplished in these cells in a length of sealed-off tubing through which the cell had initially been sealed to the vacuum line. The cells used in sets II and III had volume-calibrated necks graduated in 0.05-ml. units which permitted interpolation to 0.01 ml. Measurement of volume was precise to about $\pm 0.02\%$ in the cells used in sets I and III and to about $\pm 0.2\%$ in the cells used in set II. Sample weights were measured on a microbalance¹⁷ using 50-mg. samples in sets I and III and 15- to 20-mg. samples in set II. This provided a precision of at least $\pm 0.05\%$. Large dewar flasks filled with distilled water and ice which had been washed with distilled water served as thermostats; this gave a temperature constant to $\pm 0.002^\circ$. In all measurements cells were immersed in these baths so that menisci were 1 cm. below the upper surface of the bath. No corrections were made for solvent conductivity since this was negligible compared to the conductivities of the solutions employed.

Treatment of Data

The computational procedure used to calculate the isotope effect on the ionization of triphenylmethyl chloride¹⁰ provides a ratio of equilibrium constants $K_{\text{exp}}^{12}/K_{\text{exp}}^{13}$. These constants are functions of ionization constants, K_1 , and dissociation constants, K_2 .



$$K_{\text{exp}} = K_1 K_2 / (1 + K_1) \quad (2)$$

Of these, only K_1 changes with isotopic substitution; K_2 is a function of ion size and so is the same for labeled and unlabeled triphenylmethyl chloride. Since the ionization constant, K_1 , for triphenylmethyl chloride is of the order of 1.5×10^{-2} , and since $K_{\text{exp}}^{12}/K_{\text{exp}}^{13}$ differs from unity by only 1% (see below), the ratio K_1^{12}/K_1^{13} will be different from $K_{\text{exp}}^{12}/K_{\text{exp}}^{13}$ by an amount (0.0001) less than the precision of these experiments (± 0.0026). In the subsequent discussion, therefore, the isotope effect will be designated simply as K_{12}/K_{13} .

The data of set I were all obtained in a single cell of

(17) We are indebted to Professor C. G. Swain for the use of a microbalance in his laboratory at the Massachusetts Institute of Technology.

known constant, and they were reduced explicitly to individual equilibrium constants through the use of Shedlovsky's equation¹⁸

$$K = \frac{[S(Z)\Delta f_m]^2}{V\Delta_0[\Lambda_0 - \Delta S(Z)]} \quad (3)$$

Activity coefficients were calculated by the Debye-Hückel method using Bjerrum's q , 19.92 Å,^{10,11} as the distance parameter. K_{12} and K_{13} were then obtained separately by averaging appropriate constants. The data of sets II and III were obtained in six cells of each type (*cf.* *Conductance Measurements* above) whose cell constants were not determined. The isotope effect K_{12}/K_{13} was calculated directly from the data for each cell using eq. 15 of ref. 10. Average experimental values for each set of measurements are presented in Table I. The grand mean of these three average values was calculated by weighting each average in inverse proportion to the square of its standard deviation, and the standard deviation of the grand mean was calculated in the usual way.¹⁹

These values of the isotope effect on the ionization of triphenylmethyl chloride compare the normal substrate with one which is a mixture of triphenylmethyl- C^{13} chloride (65.6 mole %) and normal triphenylmethyl chloride (34.4 mole %). They can be transformed to ratios for 100 mole % triphenylmethyl- C^{13} chloride by use of the relationship

$$\frac{K_{12}}{K_{13}} = \frac{(K_{12}/K_{13})_{\text{obsd}}}{1 + R[1 - (K_{12}/K_{13})_{\text{obsd}}]} \quad (4)$$

Here R is the ratio of carbon-12 to carbon-13 at the labeled position of triphenylmethyl- C^{13} chloride, and $(K_{12}/K_{13})_{\text{obsd}}$ is the experimentally observed isotope effect for the incompletely labeled substrate. The derivation of eq. 4 follows directly from the operational definition of the equilibrium constant measured in solutions of the mixture of labeled and unlabeled substrate

$$(K_{13})_{\text{obsd}} = \frac{\overline{(R_{12}^+Cl^-)} + \overline{(R_{13}^+Cl^-)}}{\overline{(R_{12}Cl)} + \overline{(R_{13}Cl)}} \quad (5)$$

with the assumption that

$$\frac{K_{\text{exp}}^{12}}{K_{\text{exp}}^{13}} = \frac{K_1^{12}}{K_1^{13}} \quad (6)$$

within the accuracy of this work (see above). It neglects the carbon-13 content (natural abundance, 1.1%) of the unlabeled material. This method gives an iso-

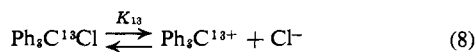
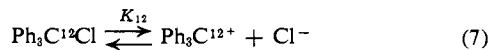
(18) T. Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

(19) A. G. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 196.

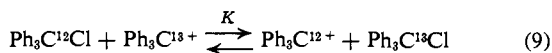
tope effect of 0.9833 ± 0.0032 (K_{12}/K_{13}) for the ionization of triphenylmethyl chloride.

Calculation of the Isotope Effect

The ionization reactions for the two isotopic species of triphenylmethyl chloride



can be combined to form an isotope exchange reaction



The equilibrium constant for this reaction is the isotope effect

$$K = K_{12}/K_{13} \quad (10)$$

It can be expressed in terms of "reduced" partition functions, f , as defined by Bigeleisen and Mayer²⁰

$$K_{12}/K_{13} = f_{\text{Ph}_3\text{C}^{12}\text{Cl}}/f_{\text{Ph}_3\text{C}^{13}\text{Cl}} \quad (11)$$

$$(s_{13}/s_{12})f = \frac{\prod_{i=1}^{3N-6} \nu_{13i}(1 - e^{-u_{13i}})e^{u_{13i}/2}}{\prod_{i=1}^{3N-6} \nu_{12i}(1 - e^{-u_{12i}})e^{u_{12i}/2}} \quad (12)$$

$$u_i = hc\nu_i/kT \quad (13)$$

Here, N is the number of atoms in the molecule to which f refers, s is its symmetry number, and ν_i are the vibrational frequencies of its normal modes in units of cm^{-1} . In the present case, isotopic substitution does not change the symmetry of either reactant or product, and the symmetry number ratios are unity. The first product on the right side of eq. 12 can also be expressed in terms of molecular masses, M , atomic masses, m , and principal moments of inertia, I_A , I_B , and I_C , through application of the Teller-Redlich product rule.

$$\frac{\prod_{i=1}^{3N-6} \nu_{13i}}{\prod_{i=1}^{3N-6} \nu_{12i}} = \left(\frac{I_{A(13)}I_{B(13)}I_{C(13)}}{I_{A(12)}I_{B(12)}I_{C(12)}} \right)^{1/2} \left(\frac{M_{13}}{M_{12}} \right)^{3/2} \left(\frac{m_{12}}{m_{13}} \right)^{3/2} \quad (14)$$

These equations make it possible to calculate the equilibrium constant for an isotope exchange reaction exactly, provided only that the frequencies of all the normal vibrational modes of each molecule participating in the reaction are known. But these data are seldom at hand for a molecule of any size or complexity. In the present case, a number of vibrational frequencies of triphenylmethyl chloride and triphenylcarbonium ion and their α -carbon-13 analogs have been assigned, but this analysis is not complete.²¹ Equation 11 will not, of course, give the correct result if only some vibrational frequencies are included, and an exact calculation of the isotope effect is not possible in the present case.

As a substitute for exact calculation of the carbon-13 isotope effect on the equilibrium ionization of triphenylmethyl chloride, we have performed a number of calculations on model systems using simplified "molecules" to represent the species of eq. 9. In these calculations, vibrational frequencies of all the normal modes of the

simplified molecules were evaluated exactly. These frequencies were then used to calculate reduced partition functions, f , and the reduced partition functions were combined into isotope effects. Vibrational frequencies were evaluated by the usual kind of normal coordinate calculation; an IBM 7090 computer program, written by Schachtschneider²² and modified by Wolfsberg,²³ was used. The input data which this program requires are force constants, bond lengths, and bond angles. Values of these parameters were chosen which correspond as closely as possible to reality; some of the criteria for these choices will be described below.

Model Systems. A theoretical investigation of the factors underlying isotope effects shows that the magnitude of primary isotope effects is governed chiefly by changes in force constants of bonds made directly to the isotopically substituted atom.²³ To a good approximation, therefore, primary isotope effects can be understood by considering only the isotopically substituted atom and those atoms which are bound directly to it. (Additional support of this assumption comes from the success of the calculations described below.) In this work we have chosen simplified molecules which conform to this approximation: as a model for triphenylmethyl chloride, we used the XY_3Z "molecule" C_3CCl and for triphenylcarbonium ion, the XY_3 "molecule" C_3C .

No detailed structural information is available for triphenylmethyl chloride, but there is no reason to believe it has abnormal geometry. We therefore assumed tetrahedral symmetry for C_3CCl with carbon-carbon bond distances of 1.54 Å and a carbon-chlorine bond distance of 1.76 Å. Structural information is available for triphenylcarbonium ion: an X-ray diffraction study of triphenylmethyl perchlorate has been made.²⁴ This work shows that the three central carbon-carbon bonds of triphenylcarbonium ion are coplanar with bond lengths of 1.417 ± 0.015 Å and bond angles of $120 \pm 2^\circ$. The same geometry was assumed for C_3C .

In the frequency calculations, simple valence force fields with no interaction force constants were used. The potential energy function which was employed for the reactant model, C_3CCl , is

$$2V = f_d(d_1^2 + d_2^2 + d_3^2) + f_D D^2 + f_\alpha(\alpha_1^2 + \alpha_2^2 + \alpha_3^2) + f_\beta(\beta_1^2 + \beta_2^2 + \beta_3^2) \quad (15)$$

Here d and D are the deviations from equilibrium positions for a C-C bond and a C-Cl bond, respectively, and α and β are similar deviations for C-C-C and C-C-Cl angles. This specifies f_d and f_D as C-C and C-Cl stretching force constants, respectively, and f_α and f_β as C-C-C and C-C-Cl bending force constants. The potential energy function which was used for the product model, C_3C , is

$$2V = f_d^+(d_1^2 + d_2^2 + d_3^2) + f_\alpha^+(\alpha_1^2 + \alpha_2^2 + \alpha_3^2) + f_\gamma^+(\gamma_1^2 + \gamma_2^2 + \gamma_3^2) \quad (16)$$

Here d is the deviation from the equilibrium position

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(21) A. Tsukamoto, R. E. Weston, Jr., and N. N. Lichtin, *Spectrochim. Acta*, to be published.

for a C-C bond, α is the deviation from the equilibrium position for a C-C-C angle in the plane of the molecule, and γ is the angular deviation of a terminal atom from the plane defined by the other three atoms. The force constant f_d^+ , then, refers to C-C stretching, and f_α^+ and f_γ^+ refer to in-plane and out-of-plane bending, respectively.

Seven force constants are needed for the calculation of vibrational frequencies using these potential energy functions. These were selected by analogy with related molecules wherever possible. Stretching force constants for the reactant model, f_d and f_D , were chosen with the help of standard compilations.^{22, 25, 26} Two values for each were selected, $f_d = 4.00$ and 4.50 mdynes/Å. and $f_D = 3.00$ and 3.40 mdynes/Å., and calculations were performed using these in different combinations. Choice of a stretching force constant for the product model, C_3C , was less straightforward because no complete vibrational analysis has been carried out on a molecule containing a positively charged carbon which is attached to other carbons by trigonal bonds. A partial analysis of the infrared spectrum of trimethyl- and dimethylcarbonium ions, however, indicates that this force constant should be larger than the corresponding force constant for paraffinic hydrocarbons.²⁷ Consideration of the length of the C-Ph bonds in triphenylcarbonium ion leads to the same conclusion: these bonds were found to be 1.42 Å. long,²⁴ which is much shorter than the length of a normal C-C bond (1.54 Å.) and nearly as short as a C-C bond in benzene (1.40 Å.). An estimate using Gordy's version²⁸ of Badger's rule indicates that the force constant for a C-C bond of this length should be 40% larger than that for a C-C bond of 1.54 Å. This agrees quite well with the 35% increase found in the work on trimethyl- and dimethylcarbonium ions.²⁷ Consequently, a value of 6.30 mdynes/Å. was chosen for the calculations of the vibrational frequencies of the product model, C_3C . This value, however, produced stretching frequencies which were considerably higher than the tentative assignments made for C-Ph stretching in the triphenylcarbonium ion,²¹ and some calculations were therefore made using the lower value of 5.00 mdynes/Å.

The choice of appropriate bending force constants was somewhat more difficult because considerable variation appears in the reported values of these. Fortunately, bending force constants are an order of magnitude smaller than stretching force constants, and errors in their estimation are likely to have a smaller effect on isotope effect calculations. In a vibrational analysis of a series of alkyl halides and related substances,²⁶ nearly identical values of C-C-C and C-C-Cl bending force constants were successful; these force constants were therefore set equal to one another in the present work ($f_\alpha = f_\beta$). A value of 0.22 mdyne/Å. for f_α/d^2 was used in most of the calculations, but, since this is only half the value used in the analysis of a number of saturated hydrocarbons,²² a few calculations were also done with $f_\alpha/d^2 = f_\beta/dD = 0.44$ mdyne/

Å. Selection of bending force constants for the product model, f_α^+ and f_γ^+ , is again attended by the difficulty that no vibrational analysis has been done on a sufficiently similar molecule. The closest analog to triphenylcarbonium ion for which this is available is isobutene, and here an in-plane bending force constant (f_α^+/d^2) of 0.68 mdyne/Å. and an out-of-plane bending force constant (f_γ^+/d^2) of 0.62 mdyne/Å. were used.²⁹ These two values are nearly equal, which is also true for the in-plane and out-of-plane bending force constants of alkylcarbonium ions.²⁷ On the other hand, in a series of planar tetratomic molecules, the out-of-plane bending force constant is consistently larger than the in-plane bending force constant and is, moreover, 0.1 to 0.2 times the stretching force constant.³⁰ Because of these uncertainties, a number of values ranging from 0.22 to 0.90 mdyne/Å. were used for these force constants in the present calculations; these values were used in combinations which included $f_\alpha^+ = f_\gamma^+$ as well as $f_\alpha^+ < f_\gamma^+$.

Vibrational Frequencies and Isotope Effects of the Model Systems. The vibrational frequencies calculated for these model systems are presented in Table II and the reduced partition functions in Table III. The infrared spectra of triphenylmethyl chloride and triphenylcarbonium ion as well as their α -carbon-13 analogs have been measured, and a number of frequency assignments have been made.²¹ Some comparison of the calculated frequencies with observed values is therefore possible. In making these comparisons, however, it should be borne in mind that off-diagonal force constants (those corresponding to interactions between internal coordinates) were neglected in the calculations. Off-diagonal force constants are generally much smaller than diagonal force constants, and the effect of this neglect on partition function ratios is probably not important. It may, however, introduce significant errors (of the order of a few per cent) in the calculated frequencies.

For the "molecule" C_3CCl , the calculated frequencies for all models except R5 (Table II) agree fairly well with measured frequencies. (R5 is the only model in which the bending force constant f_α was assigned the higher value 0.44 mdyne/Å. The lack of agreement seems to indicate that this value is too large.) The C-Ph stretching frequency in triphenylmethyl chloride has been assigned the value 1211 cm^{-1} with a lowering of 30 cm^{-1} upon carbon-13 substitution. This agrees well with the calculated values of ν_4 and its isotopic shifts in all models but R5. Apparently ν_2 is predominantly a C-Cl stretching vibration; calculated values are 5-15% lower than the assignment of 735 cm^{-1} , but the calculated isotopic shift of 3-5 cm^{-1} agrees well with the measured one of 5 cm^{-1} . The assignment of bending frequencies is very tentative, but, again, except in R5, ν_3 and ν_5 are close to the observed frequency at 311 cm^{-1} . One comparable compound for which skeletal vibrations have been assigned is *t*-butyl chloride.³¹ The symmetric C-C stretch has been placed at 1159 cm^{-1} (cf. ν_1), the degenerate C-C stretch at 1240 cm^{-1} (cf. ν_4), the C-Cl stretch at 570

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cm.⁻¹ (cf. ν_2), and skeletal bends at 304, 372, and 406 cm.⁻¹ (cf. ν_3 , ν_5 , and ν_6).

Table II. Vibrational Frequencies for Model Reactants and Products

Reactant model	Force constants, mdynes/Å.			Vibrational frequencies, cm. ⁻¹					
	f_a	f_α/d^2	f_D	ν_1 (a ₁)	ν_2 (a ₁)	ν_3 (a ₁)	ν_4 (e)	ν_5 (e)	ν_6 (e)
R1	4.00	0.22	3.00	1033	632	286	1189	335	256
				1006	628	286	1160	333	255
R2	4.00	0.22	3.40	1058	649	289	1189	335	256
				1030	646	289	1160	333	255
R3	4.50	0.22	3.00	1068	649	286	1256	336	256
				1042	644	286	1226	334	255
R4	4.50	0.22	3.40	1090	669	290	1256	336	256
				1062	664	290	1226	334	256
R5	4.50	0.44	3.40	1150	697	373	1298	463	360
				1118	693	373	1264	461	359
Product model	f_a^+	f_α^+/d^2	f_γ^+/d^2	ν_1 (a ₁)	ν_2 (a ₂)	ν_3 (e)	ν_4 (e)		
P1	5.00	0.22	0.60	841	583	1364	377		
				841	566	1330	375		
P2	6.30	0.22	0.60	944	583	1522	379		
				944	566	1485	377		
P3	5.00	0.60	0.60	841	583	1433	592		
				841	566	1394	591		
P4	6.30	0.22	0.90	944	714	1522	379		
				944	693	1485	377		
P5	6.30	0.60	0.60	944	583	1582	602		
				944	566	1540	601		

Table III. Reduced Partition Function Ratios and Calculated Values of K_{12}/K_{13} at 0° for Various Model Systems^a

Product model	f_P	Reactant model				
		R1	R2	R3	R4	R5
		1.1708	1.1741	f_R 1.1808	1.1841	1.2121
P1	1.1628	1.0069	1.0097	1.0155	1.0183	1.0424
P2	1.1852	0.9878	0.9906	0.9963	0.9991	1.0227
P3	1.1881	0.9854	0.9882	0.9939	0.9966	1.0202
P4	1.1950	0.9797	0.9825	0.9881	0.9909	1.0143
P5	1.2096	0.9679	0.9706	0.9762	0.9789	1.0021

^a The values in the body of the table are $K_{12}/K_{13} = f_R/f_P = f_{C_3CCl}/f_{C_3C}$; boldface values are within one standard deviation and italicized values are within two standard deviations of the measured isotope effect (0.9833 ± 0.0032).

For the "molecule" C_3C , agreement between calculated frequencies and those observed for triphenylcarbonium ion is less good. In models P2, P4, and P5, which use the value of the C-C stretching force constant estimated from the bond length, ν_3 is much larger than the assignment at 1359 cm.⁻¹. But the observed isotopic shift for this band, 17 cm.⁻¹, is less than half the calculated value, and this may indicate an error in assignment. (It is, in fact, difficult to account for the observed isotope effect if this shift is as small as 17 cm.⁻¹.) Frequencies were observed in triphenylcarbonium ion at 658 and 701 cm.⁻¹ which may correspond to ν_2 or ν_4 , although again the observed isotopic shifts were less than those calculated. The other calculated frequencies are in regions containing many phenyl group vibrations and so cannot be compared at all uniquely with observed values.

It is useful, before proceeding to a consideration of calculated isotope effects, to examine the effect of a drastic change in model system geometry on the vi-

brational frequencies and on the reduced partition functions. In order to do this, calculations were made with a single set of force constants for a tetrahedral configuration of C_3CCl and the configuration in which all carbon atoms are in the same plane. This change in geometry produced an appreciable change in vibrational frequencies, but it had almost no effect on the reduced partition function; the latter changed by only 0.1%. Thus, even large changes in geometry can be expected to have little influence on the isotope effect, and structural changes unaccompanied by other molecular changes cannot produce appreciable isotope effects.

The isotope effects presented in Table III are ratios of reduced partition functions of the various reactant and product models taken in all possible combinations. These reduced partition functions were calculated according to eq. 12, but of course the factors $\prod_{i=1}^{3N-6} \nu_{13i}/\nu_{12i}$ could have been evaluated from eq. 14. Since geometries were not changed in the various models, these factors must be the same for all isotope effects in Table III, and it is not necessary to calculate these factors separately for each choice of force constants. This fact points out a difference between the model system and the real system which could be a source of error in the calculations.

The model system is much smaller than the real system. Its molecular masses and moments of inertia are therefore relatively sensitive to isotopic substitution whereas those of the real system are not.³ In the real system, the molecular masses and moments of inertia contribute a factor of only 0.9995 to the isotope effect (K_{12}/K_{13}), but in the model system, this factor is 0.9893. It might, therefore, be supposed that the isotope effects obtained from the reduced partition functions for the model system should be corrected by $0.9893/0.9995 = 0.9898$ before they are compared to the observed value. Calculations in other model systems have shown, however, that secondary changes in molecular mass (changes at positions removed from the reaction center by two or more bonds) do not have a significant effect on the reduced partition function and cannot influence the isotope effect appreciably.²³ This suggests that in the present calculations molecular masses and moments of inertia from the real system should not be combined with vibrational contributions to the isotope effect supplied by the model systems.

This matter was examined explicitly for the present case by making calculations on enlarged models. For both reactant and product, additional atoms, X, were placed on extensions of the C-C bond to give $(XC)_3CCl$ as the new reactant model and $(XC)_3C$ as the new product model. In both new models the C-C-X angle was 180° and a C-C-X bending force constant of 0.22 mdyne/Å. was assumed. In the reactant model the C-X bond length was set at 1.54 Å. and a value of 4.00 mdynes/Å. was used as the C-X stretching force constant; in the product model these quantities were 1.417 Å. and 5.00 mdynes/Å. All other force constants, bond lengths, and bond angles of the new reactant models were identical with those of reactant model R2, and in the new product model they were identical with those of the original model P3. Calculations were done in which the additional

atom, X, had masses of 12 and 100. The results of these calculations are presented in Table IV. Increasing the size of the "molecules" in the model system had, as was expected, an appreciable effect on the molecular mass-moment of inertia ratios for both reactant and product. These decreased by some 15% when the model was changed from one with no X atom present to one in which the X atom had a mass of 100, and their ratios provided contributions to the isotope effect varying from 1% to almost nothing. The reduced partition functions, however, changed by a much smaller amount, and since the changes for reactant and product were parallel as the model varied, the isotope effect changed by only 0.04%. This demonstrates that, in a system consisting of small molecules whose isotope effect is known to be the same as that of a related larger system (because force constant changes are the same), the vibrational contribution to the isotope effect must offset the molecular mass-moment of inertia contribution in such a way as to compensate for the difference in molecular masses and moments of inertia of the two systems. It must be concluded, therefore, that, with regard to the present calculations of the isotope effect on the ionization of triphenylmethyl chloride, only the complete reduced partition functions for each model system are significant, and that molecular masses and moments of inertia from the real system cannot be combined with vibrational terms for the models. The constancy of the isotope effects in Table IV over such a large change in model size also provides some justification for the approach used in this investigation: grossly abbreviated models of large molecules can be used to make valid isotope effect calculations. A similar conclusion has been reached by other investigators working with other model systems.²³

Table IV. Frequency Products and Reduced Partition Function Ratios for Enlarged Models

Model	Mass of X	$\left(\frac{M_{13}}{M_{12}}\right)^{3/2} \left(\frac{I_{A(13)}I_{B(13)}I_{C(13)}}{I_{A(12)}I_{B(12)}I_{C(12)}}\right)^{1/2}$	f
C ₃ CCl	...	1.1501	1.1741
(CX) ₃ CCl	12	1.0126	1.1871
(CX) ₃ CCl	100	1.0042	1.1878
C ₃ C	...	1.1625	1.1881
(CX) ₃ C	12	1.0179	1.2015
(CX) ₃ C	100	1.0043	1.2025
C ₃ CCl/C ₃ C	...	$f(R)/f(P) = 0.9882$	
(CX) ₃ CCl/(CX) ₃ C	12	$f(R)/f(P) = 0.9880$	
(CX) ₃ CCl/(CX) ₃ C	100	$f(R)/f(P) = 0.9878$	

Although changes in size and geometry of the model system have little effect on the calculated isotope effect, changes in force constants do alter it considerably. This is readily apparent from an examination of Table III. The variation in individual force constants represented by the different models in this table is in most cases rather small: all of the force constants have "reasonable" values. And yet, the calculated isotope effect varies from a high of 1.042 to a low of 0.968. This is a variation of nearly 8%, which corresponds, on the basis of experimental experience, to the difference between no carbon-13 isotope effect and an unusually large carbon-13 effect.

The best calculated value in Table III is that for the

model system R2-P4; this isotope effect, $K_{12}/K_{13} = 0.9825$, is only 0.08% below the measured value of 0.9833. The next best calculated value is that for R1-P3 which is 0.21% above the experimental isotope effect. Both of these calculated ratios lie within one standard deviation of the measured value. Calculated isotope effects for five more model systems lie within two standard deviations of the measured value: R1-P2, R2-P3, and R3-P4 are increasingly above 0.9833 in that order, and R1-P4 and R4-P5 are increasingly below. One reactant model, R5, and one product model, P1, give isotope effects which do not correspond to that in the real system at all well; neither model can be made to produce an inverse isotope effect in combination with any of the present models. The unsatisfactory reactant model is the one in which all three force constants have the highest values used, and it is the only model in which the value of 0.44 mdyne/Å. was used for the bending force constant f_{α} . In the unsatisfactory product model, on the other hand, all three force constants have the lowest values used, even though two of these are still larger than the highest values used for corresponding force constants in the reactant models. This indicates that the observed isotope effect cannot be duplicated by calculation without using considerably larger force constants in the product than in the reactant. This conclusion is supported by the most successful model systems. In R1-P3 the product stretching force constant (f_d^+) is 1.25 times the reactant C-C stretching force constant (f_d), and product bending force constants (f_{α}^+ , f_{γ}^+) are nearly three times the reactant bending force constant (f_{α}); whereas in R2-P4, $f_d^+ = 1.57f_d$, and the average of f_{α}^+ and f_{γ}^+ is again nearly three times f_{α} .

Approximate Forms of the Partition Function Ratio. The relationship between force constants and isotope effect can be seen more clearly through the use of an approximate expression which demonstrates explicitly the connection between these two. Equation 12 can be rewritten as

$$f = \prod_{i=1}^{3N-6} \frac{u_{12i}^{-1} \sinh(u_{12i}/2)}{u_{13i}^{-1} \sinh(u_{13i}/2)} \quad (17)$$

and this can be expanded as a power series in u_i ,

$$f = \prod_{i=1}^{3N-6} \frac{u_{12i}^{-1} \left[\frac{u_{12i}}{2} + \frac{(u_{12i}/2)^3}{3!} + \frac{(u_{12i}/2)^5}{5!} + \dots \right]}{u_{13i}^{-1} \left[\frac{u_{13i}}{2} + \frac{(u_{13i}/2)^3}{3!} + \frac{(u_{13i}/2)^5}{5!} + \dots \right]} \quad (18)$$

If only the first nonvanishing terms in u_i are considered, this becomes

$$f = \prod_{i=1}^{3N-6} \frac{1 + u_{12i}^2/24}{1 + u_{13i}^2/24} \quad (19)$$

which can be approximated by

$$\ln f = \frac{1}{24} \sum_{i=1}^{3N-6} u_{12i}^2 - u_{13i}^2 \quad (20)$$

provided that u_i is small. It has been shown that the validity of eq. 20 can be extended to higher values of u_i by replacing $1/24$ with $\bar{\gamma}/24$.³²

(32) J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, 1, 16 (1958).

$$\ln f = \frac{\bar{\gamma}}{24} \sum_{i=1}^{3N-6} u_{12i}^2 - u_{13i}^2 \quad (21)$$

The correction factor $\bar{\gamma}$ can be calculated from the individual values of u_i ; it varies from unity when u_i is zero to approximately 0.3 for a frequency of 3000 cm^{-1} at 300°K. Equation 21 is equivalent to

$$\ln f = \frac{\bar{\gamma}}{24} \left(\frac{hc}{2\pi kT} \right)^2 \sum_{i=1}^{3N-6} \lambda_{12i} - \lambda_{13i} \quad (22)$$

$$\lambda_i^{1/2} = 2\pi\nu_i \quad (23)$$

where λ_i are the roots of the secular equation for harmonic motion of a system of N atoms. The sum in eq. 22 can be evaluated readily by the *FG* matrix method of Wilson.²⁵ If no interaction force constants are used, $\sum_{i=1}^{3N-6} \lambda_i$ is simply the sum of products of corresponding diagonal terms in the *F* and *G* matrices. In the difference $\sum_{i=1}^{3N-6} (\lambda_{12i} - \lambda_{13i})$, the terms which do not contain the mass of the isotopically substituted atom explicitly vanish. Thus, only that part of the molecule which contains the isotopically substituted atom and other atoms directly involved in its vibrational motions needs to be considered. Other parts of the molecule can influence the isotope effect only through their influence on $\bar{\gamma}$.

This method can be applied to the present case by using the *F* matrix elements defined by eq. 15 and 16 and the *G* matrix elements given by Wilson, Decius, and Cross.³³ This leads to the following expression for the isotope effect

$$\ln K_{12}/K_{13} = \ln f_{\text{Ph}_3\text{CCl}} - \ln f_{\text{Ph}_3\text{C}^+} = \frac{1}{24} \left(\frac{hc}{2\pi kT} \right)^2 \left(\frac{10^6}{c^2 M} \right) \times \\ (12^{-1} - 13^{-1}) [\bar{\gamma}(f_D + 3f_d + 8f_\alpha/d^2 + 8f_\beta/dD) - \\ \bar{\gamma}^+(3f_d^+ + 9f_\alpha^+/d^2 + 3f_\gamma^+/d^2)] \quad (24)$$

where $\bar{\gamma}$ refers to the reactants and $\bar{\gamma}^+$ refers to the products. In eq. 24 M is the factor for conversion of atomic mass units to grams, and force constants are in $\text{m-dynes}/\text{\AA}$. Estimates of 0.65 for $\bar{\gamma}$ and 0.60 for $\bar{\gamma}^+$ can be made from the frequencies of the reactant and product models of Table II, and f_β can be set equal to f_α since the same value was assigned to these force constants in all the model calculations. The expression for the isotope effect at 0° is then

$$\ln K_{12}/K_{13} = 0.0125[0.65(f_D + 3f_d + 16f_\alpha/d^2) - \\ 0.60(3f_d^+ + 9f_\alpha^+/d^2 + 3f_\gamma^+/d^2)] \quad (25)$$

Equation 25 shows that an inverse isotope effect in this system must be the result of stronger force constants in the product than in the reactant. If, for example, the assumption is made that the product force constants have the same values as corresponding reactant force constants ($f_d^+ = f_d$, $f_\alpha^+ = f_\alpha$, $f_\gamma^+ = f_\gamma$), eq. 25 predicts an isotope effect of 3 to 4% in the normal direction ($K_{12}/K_{13} > 1.00$). This is a consequence of the fact that more force constants appear in the reactant portion of eq. 25 than in the product portion. The reactant term contains the C-Cl stretching force constant, f_D , which of course is absent from the product term. In addition, the bending force constant has a

(33) Reference 25, Appendix VI.

coefficient of 16 in the reactant term, whereas in the product term the bending force constant coefficients are only 9 and 3. To offset this, the product force constants must be considerably stronger than the reactant force constants.

Conclusions

The equilibrium ionization of triphenylmethyl chloride shows an inverse carbon-13 isotope effect of nearly 2% ($K_{12}/K_{13} = 0.983$) when isotopic substitution is made at one end of the reacting bond. This rather unusual observation might seem to place this process in a class apart from the $\text{S}_{\text{N}}1$ ionization reactions for which it was chosen to be a model: kinetic carbon isotope effects on $\text{S}_{\text{N}}1$ substitution, though small, are all in the normal direction.^{7,8} The kinetic isotope effects, however, compare covalent initial states with transition states in which ionization is occurring but is still incomplete. The equilibrium isotope effect, on the other hand, compares a covalent initial state with a final state in which ions are fully formed. Thus, whatever changes in the system ionization is producing, these changes will be incompletely realized (to various degrees) in the kinetic cases but will be completely accomplished in the equilibrium. The equilibrium, therefore, can be considered to be one extreme of a continuum. If the kinetic isotope effects are unusually small, the equilibrium isotope effect should be still smaller, and it might well be on the other side of unity. Thus, the inverse isotope effect on triphenylmethyl chloride ionization, rather than confounding the kinetic situation, supports it. This isotope effect, moreover, because it is an extreme value, holds promise of containing among its underlying factors the source of the low kinetic isotope effects in exaggerated form.

Theoretical analysis of the carbon isotope effect on the equilibrium ionization of triphenylmethyl chloride indicates that the principal cause of this inverse effect is the presence of larger C-Ph force constants in the triphenylcarbonium ion than in triphenylmethyl chloride. Since force constants measure the magnitude of the forces resisting deformation of a bond from its equilibrium configuration, they are indicative of bond strength. The conclusion supplied by the theoretical analysis can therefore be restated by saying that the present isotope effect is the result of stronger C-Ph bonds in triphenylcarbonium ion than in triphenylmethyl chloride. This increase in bond strength, moreover, must be sufficient to overcome the loss of a C-Cl bond.

The central trigonal carbon atom of triphenylcarbonium ion is conjugated with adjacent phenyl groups. This conjugation increases the order of the C-Ph bonds and makes them stronger than corresponding bonds in triphenylmethyl chloride where similar conjugation is not possible. The unusual shortness of these C-Ph bonds in triphenylcarbonium ion (1.42 \AA ., which, when compared to a normal C-C bond length of 1.54 \AA ., represents bond shortening of more than half that of an olefinic double bond over a C-C single bond) indicates that this conjugative bond strengthening is appreciable and could well compensate for the loss of a C-Cl bond.

A similar strengthening of nonreacting bonds to the carbon atom undergoing substitution can be expected

to occur in S_N1 reactions of *t*-butyl chloride and α -phenylethyl bromide, the two substances for which carbon isotope effects on S_N1 substitution have been measured. In *t*-butyl chloride, hyperconjugative interaction between the forming positive charge and adjacent methyl groups will strengthen the nonreacting C–C bonds, whereas in α -phenylethyl bromide, hyperconjugation of the positive center with the single methyl group will be aided by ordinary conjugation with the phenyl substituent. The fact that the C–C stretching force constant of the trimethylcarbonium ion is 35% stronger than the corresponding force constant in alkanes²⁷ indicates that hyperconjugative bond strengthening is appreciable. Ordinary conjugation, however, should have a stronger influence on bond strength than hyperconjugation, and this may be the reason why the isotope effect for *t*-butyl chloride is greater than that for α -phenylethyl bromide even when the former is reduced to a carbon-12:carbon-13 ratio.

It can be concluded, therefore, that carbon isotope effects in these carbonium ion-producing reactions are

low because conjugation strengthens the nonreacting bonds to the isotopically substituted atom. It is tempting to generalize these results by saying that all carbon isotope effects on S_N1 substitution will be low, but such a generalization may prove to be correct only because S_N1 substitution is commonly observed in systems where conjugative stabilization of the forming positive charge makes this kind of reaction possible. Should a system be examined in which S_N1 substitution is forced in the absence of conjugative assistance, a large isotope effect may be found, and this may in fact be the reason why the solvolysis of methyl iodide in the presence of silver ion (possibly an S_N1 reaction) shows a carbon-14 isotope effect of nearly 9%.²⁸

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The Photolysis of Phosgene–Ethylene Mixtures¹

Julian Hecklen

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Chlorine atoms were produced by the photolysis of COCl₂ with 2537-Å radiation at 23°. The atoms were quantitatively scavenged by C₂H₄, and the reactions of the resulting radicals were studied. The significant variable in the system is (C₂H₄)/I_a^{1/2}, which was varied by a factor of 10⁴. Only two radicals, C₂H₄Cl and C₄H₈Cl, are important. At high (C₂H₄)/I_a^{1/2}, the products of the less important C₆H₁₂Cl radical can also be detected. The photochemical products found were CO, 1-C₆H₁₂, C₂H₅Cl, 1-C₄H₉Cl, 1-C₆H₁₃Cl, 1,2-C₂H₄Cl₂, 1,3-C₄H₈Cl₂, 1,4-C₄H₈Cl₂, and 1,6-C₆H₁₂Cl₂. Also, another C₆ hydrocarbon, a C₄H₇Cl compound, and two C₆H₁₁Cl compounds were detected. Not detected, but surely present, were C₂H₃Cl and C₄ hydrocarbons. From the generalized propagation–termination mechanism and the behavior of the products with changes in (C₂H₄)/I_a^{1/2}, the classes of radical–radical reactions that lead to each product could be established without a detailed knowledge of the particular radical–radical reactions. This classification is listed in Table III. The detailed mechanism was deduced; in order to explain the results, it was necessary to introduce, as the principal reaction of two C₄H₈Cl radicals, the unusual reaction 2C₄H₈Cl → C₄H₇Cl + C₂H₅Cl + C₂H₄. Many ratios of rate constants were determined; they are collected in Table IV. When the free-electron ends of two radicals approach each other, either H-atom transfer or combination can occur. The ratio of the rates of the two processes is about 0.4 irrespective of the radicals. On the other hand,

Cl-atom transfer occurs from a different orientation. The evidence indicates that the ratio of Cl-atom transfer to H-atom transfer is markedly altered as the chain length of the radicals is enhanced with the heavier of the two dichlorides being preferentially produced. The ratio of the rate constant for propagation to the square root of that for termination is about 1/100th as large for the C₄H₈Cl radical as for the C₂H₄Cl radical.

Introduction

A number of studies of chlorine-atom addition to olefinic compounds have been done in recent years. The two groups of experimenters associated with Dainton and with Goldfinger have predominated the field. Their work has been concerned mainly with the initial chlorination mechanism and rates, and the reactions of the initially formed radicals with molecular chlorine. Their results and conclusions are summarized in the excellent review by Cvetanović.²

Wijnen^{3,4} has studied the reactions of the chlorinated radicals by using the elegant technique of generating chlorine atoms by the photodecomposition of phosgene. The photolysis yields quantitatively two chlorine atoms for each carbon monoxide molecule. No complicating side reactions occur. The COCl intermediate is too unstable at room temperature and

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