

Two different preparations of each chloride were used and three different types of conductivity cells were employed. The average of ionization constants for 22 determinations was 0.9890,  $\sigma = 0.0021$ ,<sup>6</sup> ( $\sigma$  is standard deviation of mean value) which corresponds to an isotope effect ( $K_{12}/K_{13}$ ) of 0.9833,  $\sigma = 0.0031$ , for the completely labeled substance.

The probable source of this inverse isotope effect can be deduced by considering the mechanical properties of the chemical species involved in the ionization of triphenylmethyl chloride. The isotope effect can be expressed in the usual way as a ratio of partition functions and differences in zero-point energy for the isotopically substituted reactants and products. This reduces to an expression consisting of symmetry numbers,  $s$ , molecular masses,  $M$ , moments of inertia,  $A$ ,  $B$ ,  $C$ , and vibrational frequencies,  $\omega$  ( $u = hc\omega/kT$ )

$$\frac{K_{12}}{K_{13}} = \left(\frac{s_{12}}{s_{13}}\right)_R \left(\frac{s_{12}}{s_{13}}\right)_P \left(\frac{M_{12}}{M_{13}}\right)_R^{1/2} \left(\frac{M_{12}}{M_{13}}\right)_P^{1/2} \times \left(\frac{A_{13}B_{13}C_{13}}{A_{12}B_{12}C_{12}}\right)_R^{1/2} \left(\frac{A_{13}B_{13}C_{13}}{A_{12}B_{12}C_{12}}\right)_P^{1/2} \prod_i^{3n-6} \left(\frac{\sinh u_i(12)/2}{\sinh u_i(13)/2}\right)_R \times \prod_i^{3n-6} \left(\frac{\sinh u_i(13)/2}{\sinh u_i(12)/2}\right)_P \quad (1)$$

Isotopic substitution does not alter the symmetry of either reactant or product, and the product of the symmetry number ratios is unity. The mass ratios contribute a factor of 0.9992 to the isotope effect. The moments of inertia of the product are not affected by isotopic substitution: the product is a symmetrical carbonium ion in which isotopic change is made at the center of mass. One of the principal moments of inertia of the reactant is also non-isotopic; the other two contribute a factor of 1.0003. This is for a triphenylmethyl chloride molecule with regular tetrahedral bonds about the central carbon atom and normal bond angles and bond lengths elsewhere. Use of any other reasonable model will not produce a significant change in this number. The combined effect of these terms of eq. 1—the non-vibrational component of the isotope effect—is a factor of 0.9995. This accounts for only 5% of the observed effect. Essentially all of this isotope effect therefore must be due to differences in vibrational frequencies.

Triphenyl carbonium ion has one atom and three vibrational degrees of freedom less than triphenylmethyl chloride. The observed inverse isotope effect, however, demands that the sum of the vibrational frequencies of the normal modes in the carbonium ion be greater than the sum for the chloride. Some vibrations in the ion, then, must be tighter than corresponding ones in the chloride by an amount sufficient to offset the effect of fewer vibrations, and the carbonium ion must have some bonds which are stronger than corresponding bonds in the chloride. An X-ray diffraction investigation of the structure of triphenylmethyl perchlorate shows that the carbon-phenyl bond in the carbonium ion is indeed 0.10 Å. shorter than the normal carbon-carbon single bond distance.<sup>7</sup> Badger's rule<sup>8</sup> predicts that the force constant of this shortened bond will be some 40% larger than the force constant of the carbon-phenyl bond in triphenylmethyl chloride. The effect of this increase in force constant on the vibrational frequencies is difficult to assess quantitatively, because vibrations of a molecule as complex as those being considered here cannot be treated as stretching and bending modes of single bonds. The frequencies of

(6) This value was obtained by weighting the mean ratios determined in each of the three types of cells in proportion to the reciprocals of the squares of their standard deviations: 0.9876,  $\sigma = 0.0061$  ( $n = 6$ ); 0.9866,  $\sigma = 0.0043$  ( $n = 8$ ); and 0.9901,  $\sigma = 0.0026$  ( $n = 8$ ).

(7) K. Eriks and A. Gomez de Mesquita, personal communication.

(8) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).

a number of normal modes will be changed, and a quantitative estimate of these changes requires a complete vibrational analysis. Changes large enough to account for the observed isotope effect of 1.7% are reasonable, however, by analogy with the equilibrium dissociation of the boron trifluoride-dimethyl ether complex. An inverse isotope effect of 3% ( $B^{10}/B^{11}$ ) in this system has been attributed to vibrational changes accompanying a shortening of the boron-fluorine bond from 1.43 Å. in the complex to 1.295 Å. in boron trifluoride.<sup>9</sup>

This analysis suggests that the principle source of the inverse isotope effect of 1.7% on the ionization of triphenylmethyl chloride is the increased strength of carbon-phenyl bonds in the triphenyl carbonium ion. Isotopic substitution, occurring as it does near the center of a large molecule, has very little effect on molecular masses and moments of inertia. In an SN1 reaction these non-vibrational contributions to the isotope effect are also likely to be small: pure SN1 reactions have not been realized with very small molecules. SN1 reactions are, moreover, most common in systems where some stabilization of the intermediate carbonium ion is possible, and this usually takes the form of resonance stabilization of the positive charge. Such charge delocalization strengthens the bonds to the reacting carbon which are not being broken, and this strengthening offsets the loss in bonding produced by bond-breaking. Thus, in the solvolysis of *t*-butyl chloride, hyperconjugation strengthens the carbon-methyl bonds in the forming carbonium ion. This effect is not, of course, as large as that in the triphenyl carbonium ion, but it is enough to reduce the vibrational contribution to the isotope effect. The combination of these effects, a vanishing contribution from the non-vibrational parts of the isotope effect and a diminished vibrational contribution serves to produce a small isotope effect in those systems where SN1 reactions are most likely.

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(9) A. A. Palko, G. M. Begun and L. Landau, *ibid.*, **37**, 552 (1962).

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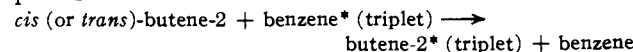
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#### THE RADIATION INDUCED *cis-trans* ISOMERIZATION OF BUTENE-2

Sir:

The precise roles of electronic energy transfer, free radical reactions and charge or electron transfer in radiolyses are still uncertain. Van Dusen and Hamill<sup>1</sup> have pointed out that scintillation experiments demonstrate that singlet states are chemically unimportant in energy transfer processes induced by ionizing radiation. The possibility of triplet participation remains, but spectroscopic or other conclusive evidence has been lacking.

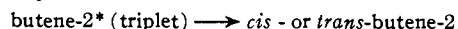
Olefins are very effective quenchers of the triplet state of benzene<sup>2</sup> and if pure *cis-* or *trans*-butene-2 is used for this purpose, isomerization results from the process



(1) W. Van Dusen and W. H. Hamill, *J. Am. Chem. Soc.*, **84**, 3648 (1962).

(2) R. B. Cundall and D. G. Milne, *ibid.*, **83**, 3902 (1961).

followed by



with equal probability. We have used this reaction to assess the yield of benzene triplets under different conditions of irradiation.

Benzene solutions with varying concentrations of *cis*-butene-2 were irradiated with  $\gamma$ -rays from a 500-curie cobalt-60 source. Considerable isomerization of the butene-2 was observed, the  $G(\text{trans-C}_4\text{H}_8\text{-2})$  values ranging from 0.18 to 2.3, the latter being the value for all solutions with butene-2 concentrations greater than 0.1 *M*. Energies absorbed were measured by the Fricke dosimeter ( $G_{\text{F}_2^{3+}} = 15.6$ ).

No isomerization was observed when similar experiments were carried out in *n*-hexane. However, when mixtures of *n*-hexane, benzene and *trans*-butene-2 were irradiated, even though the  $G(\text{H}_2)$  values decreased with increasing benzene concentration due to the latter's protective action, the  $G(\text{cis-C}_4\text{H}_8\text{-2})$  values increased to that for pure benzene solutions.

When iodine was introduced into the benzene-*cis*-butene-2 system, the  $G(\text{trans-C}_4\text{H}_8\text{-2})$  values decreased slightly but the side products found in iodine-free systems were absent. This, combined with the evidence from the hexane experiments, rules out the possibility of the isomerization proceeding by a free radical mechanism.

Mixtures of cyclohexene, benzene and *cis*-butene-2 also were examined and as in the hexane experiments  $G(\text{H}_2)$  values dropped with increasing mole fraction of benzene while the  $G(\text{trans-C}_4\text{H}_8\text{-2})$  values increased from 0 for pure cyclohexene to 0.55 for a 3:1 benzene-cyclohexene mixture. The isomerization does not proceed *via* a charge transfer mechanism since this would be enhanced by increasing cyclohexene concentration.<sup>3</sup>

If the isomerization takes place by an energy transfer mechanism involving the benzene triplet, another material with a triplet energy lower than those of both benzene and butene-2 should decrease the amount of isomerization. The addition of anthracene to benzene *cis*-butene-2 solutions lowered the  $G(\text{trans-C}_4\text{H}_8\text{-2})$  values.

The data obtained are exemplified in Table I.

(3) J. Manlon and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952).

TABLE I

THE RADIATION INDUCED *cis-trans* ISOMERIZATION OF BUTENE-2

Solution	Mole fraction of benzene	Concn. of butene-2 moles/l.	$G(\text{H}_2)$	$G(\text{C}_4\text{H}_8\text{-2})$ isomerization
Pure benzene		0.0027( <i>cis</i> )	0.0375	1.18( <i>trans</i> )
		.047 ( <i>cis</i> )	.038	1.33( <i>trans</i> )
		.122 ( <i>cis</i> )	.038	2.30( <i>trans</i> )
		.179	.038	2.29( <i>trans</i> )
Benzene-hexane	0	.018( <i>trans</i> )	3.93	— ( <i>cis</i> )
	0.593	.033( <i>trans</i> )	0.52	0.31( <i>cis</i> )
	.814	.018( <i>trans</i> )	.28	1.05( <i>cis</i> )
Benzene + I <sub>2</sub> (0.0076 g. mole. l. <sup>-1</sup> )		.03 ( <i>cis</i> )	.038	0.89( <i>trans</i> )
		.13 ( <i>cis</i> )	.038	1.90( <i>trans</i> )
Cyclohexene-benzene	0	.27 ( <i>cis</i> )	1.20	— ( <i>trans</i> )
	0.276	.27 ( <i>cis</i> )	0.77	— ( <i>trans</i> )
	.533	.27 ( <i>cis</i> )	.44	— ( <i>trans</i> )
	.774	.27 ( <i>cis</i> )	.3	0.55( <i>trans</i> )
Benzene-anthracene (0.056 g. mole. l. <sup>-1</sup> )		.0475( <i>cis</i> )	.038	0.50( <i>trans</i> )
	<sup>a</sup>	.0475( <i>cis</i> )	.038	1.48( <i>trans</i> )
		.0924( <i>cis</i> )	.038	0.85( <i>trans</i> )
	<sup>a</sup>	.0924( <i>cis</i> )	.038	2.30( <i>trans</i> )
	<sup>a</sup>	.118 ( <i>cis</i> )	.038	1.10( <i>trans</i> )
<sup>a</sup>	.118 ( <i>cis</i> )	.038	2.30( <i>trans</i> )	

<sup>a</sup> Pure benzene.

These experiments demonstrate that large amounts of benzene triplets are formed during irradiation of benzene and that the  $G(\text{C}_6\text{H}_6 \text{ triplet})$  must be about 4.60, a value comparing very closely with  $G(\text{H}_2)$  for pure *n*-hexane (4.0).<sup>4</sup> The protective action of the benzene evidently involves processes producing the triplet state of benzene. The specific sensitizing effect of the benzene makes an electron transfer mechanism<sup>5</sup> for the isomerization unlikely. The work is being extended.

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(4) W. H. T. Davison, *Chem. Ind. (London)*, 662 (1957).

(5) J. H. Baxendale and F. W. Mellows, *J. Am. Chem. Soc.*, **83**, 4720 (1961).

## BOOK REVIEWS

**The Chromatography of Steroids.** By I. E. BUSH, M.A., Ph.D., M.B., B.Ch. (Cantab.), Bowman Professor of Physiology, The University of Birmingham. Pergamon Press Ltd., Headington Hill Hall, Oxford, England. 1961. xxi + 437 pp. 16 × 23.5 cm. Price, \$12.50.

This monograph despite its general title deals primarily with paper chromatography. Column chromatography is adequately treated but the newer techniques of thin layer and vapor phase chromatography are not covered at all. The author has departed from the conventional description of techniques, solvent systems and mobilities and instead has approached the subject mainly from the theoretical point of view. One of the author's aims was "to show that the behavior of steroids in chromatographic systems is a consequence of general laws and that it can be treated quantitatively with reasonable accuracy." For this purpose nearly half of the book is devoted to the basic theory of chromatography, the quantitative treatment of chromatographic behavior of steroids and the use of chromatography for structure analysis. The chapter on techniques and apparatus is very informative and includes many innovations introduced by the author. Methods for the preparation of ex-

tracts for chromatography are also found in this chapter. There is a chapter on various colorimetric and radioactive techniques for quantitation including the direct scanning of paper chromatograms, both manual and automatic. Typical analytical problems in steroid biochemistry such as hydrocortisone in human blood and urinary steroids are dealt with in a special chapter. The appendices are full of useful information on purification of reagents and materials, microchemical reaction and methods for detection.

The theoretical and quantitative treatment of organic compounds in chromatographic systems, has been studied in other fields. The author believes, and the reviewer agrees, that further extension of these studies would be very fruitful in the field of steroids with the variety and number of functional groups and known stereochemistry. The term  $R_M$ , defined earlier by Bates-Smith and Westall as  $R_M = \log(1/R_F - 1)$  is introduced into steroid chromatography. Theoretically, the change in  $R_M$  is a constant. The  $\Delta R_M$  due to substitution (H → R) or due to reaction (*i.e.*, OH → = O) at a given position was found to be reasonably constant in a given solvent system for a series of steroids where reliable  $R_F$  values were available. Similarly, the  $\Delta R_M$  due to a change in solvent systems for a particular group was