experiment in which phenylmercuric bromide was treated with potassium chloride in a solvent mixture consisting of *tert*-butyl alcohol, chloroform and benzene for 4 hr. with high speed stirring, no halide exchange producing phenylmercuric chloride was observed. In addition, phenyl-(bromodichloromethyl)-mercury,[4] prepared by the above reaction in which bromodichloromethane was used in place of chloroform, was shown to be inert toward chloride ion under similar conditions.

These results speak strongly against a dihalocarbene insertion mechanism for the reaction of phenylmercuric chloride with haloforms and potassium *tert*-butoxide. Were such a mechanism to obtain, phenyl-(bromodichloromethyl)-mercury would be the product expected in the phenylmercuric bromide–chloroform–potassium *tert*-butoxide reaction in view of the demonstration that neither phenylmercuric bromide nor phenyl-(bromodichloromethyl)-mercury undergo exchange with chloride ion under the conditions used. Our results indicate that the formation of the phenyl-(trichloromethyl)-mercurial isolated proceeded by simple nucleophilic displacement of bromide ion by the trichloromethyl anion. Hine[5] demonstrated the intermediacy of this anion in the formation of dichlorocarbene by the basic hydrolysis of chloroform, and the lifetime of such carbanion intermediates (relative to their decomposition to dihalocarbenes) is sufficiently long to allow other reactions besides dihalocarbene formation to be observed. Also pertinent is the fact that nucleophilic displacement of chloride ion from mercury in organomercuric chlorides (*e.g.*, by iodide ion[6]) is known to occur readily. It therefore is not surprising to encounter a displacement reaction such as the one demonstrated by us.

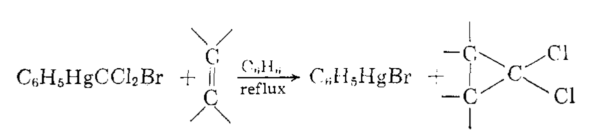
$$C_6H_5HgBr + CCl_3^- \longrightarrow C_6H_5HgCCl_3 + Br^-$$

When bromine-containing haloforms were used in this reaction, the products were those expected, *e.g.*

$$C_6H_5HgCl \xrightarrow{CHCl_2Br,\ t\text{-}C_4H_9OK} C_6H_5HgCCl_2Br$$

but the interpretation of these reactions is complicated by the fact that exchange between bromide ion (from the haloform-base reagent mixture, which is used in twofold excess) and phenylmercuric chloride does occur.

The use of phenyl-(trichloromethyl)-mercury and phenyl-(tribromomethyl)-mercury in the synthesis of 1,1-dihalocyclopropanes has been reported by us.[7] It is of special interest from the synthetic standpoint that the presence of a bromine substituent in the trihalomethyl group greatly facilitates the reaction of these mercurials with olefins. Thus phenyl-(bromodichloromethyl)-mercury is far superior to phenyl-(trichloromethyl)-mercury in its reaction with olefins to produce exclusively 1,1-dichlorocyclopropanes, since reaction times of only a few hours are sufficient to give comparable (85–90%) yields in the case of the former mercurial. Phenyl-(dibromochloromethyl)-mercury[8] serves excellently as starting material for the synthesis of 1-bromo-1-chlorocyclopropanes by the same procedure. The mechanism of the phenyl-(trihalomethyl)-mercury-olefin reaction is under investigation. Details concerning these and related experiments will be reported at a later date.



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[4] M. p. 110–111°, with vigorous decomposition immediately upon melting. *Anal.* Calcd. for $C_7H_5Cl_2BrHg$: Hg, 45.53; Cl, 16.09; Br, 18.14. Found: Hg, 45.82; Cl, 15.96; Br, 17.90.

[5] J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950).

[6] D. Seyferth and R. H. Towe, *Inorg. Chem.*, **1**, 185 (1962).

[7] D. Seyferth, J. M. Burlitch and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

[8] M.p. 110–111° (dec.). *Anal.* Calcd. for $C_7H_5ClBr_2Hg$: Hg, 41.36; Cl, 7.30; Br, 32.95. Found: Hg, 41.36; Cl, 7.07; Br, 32.71.

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LARGE SECONDARY INTERMOLECULAR KINETIC ISOTOPE EFFECTS IN NON-EQUILIBRIUM SYSTEMS. ENERGIZATION BY CHEMICAL ACTIVATION

Sir:

The existence of very large, *normal*, secondary intermolecular kinetic isotope effects was pointed out recently by Rabinovitch and Current, and the quantum statistical basis of the phenomenon described.[1] These effects *may* arise quite widely in unimolecular systems in which the energized species are produced in some non-equilibrium distribution $f(\epsilon)$, *i.e.*, one in which the populations of the various energy levels of interest are not governed by the ambient temperature and statistical thermodynamic equilibrium considerations. The experimental techniques may in suitable cases include excitation by electron impact, light absorption, radiation, *etc.* In fact, thermal collisional activation may also be employed and, under conditions where non-equilibrium populations prevail (the lower pressure region of thermal unimolecular reactions), has been shown to give rise to very large *inverse* intermolecular secondary isotope effects.[2]

The above mentioned authors performed experiments involving excitation of vibrational and active rotational degrees of freedom by chemical activation,[3] in which the rates of C–H rupture of energized ethyl-d_1 and ethyl-d_3 radicals were compared at 25°, *i.e.*, $C_2H_4D^* \rightarrow C_2H_3D + H$ and $C_2H_2D_3^* \rightarrow C_2HD_3 + H$. The relative rates for this secondary isotope effect at lower pressures were $k_{d_1}/k_{d_3} \sim 2.2$, or a factor of ~ 1.5 per extra D atom. Although very large as compared with the customary effect per D atom in equilibrium unimolecular systems,[1] the total effect is below the frequently observed magnitude of C–H, C–D primary isotope effects in equilibrium[4] and non-equilibrium[5]

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[1] B. S. Rabinovitch and J. H. Current, *Can. J. Chem.*, **40**, 557 (1962).

[2] B. S. Rabinovitch, D. W. Setser and F. W. Schneider, *ibid.*, **39**, 2609 (1961).

[3] B. S. Rabinovitch and R. W. Diesen, *J. Chem. Phys.*, **30**, 730 (1959), *et seq.*

[4] L. Melander, "Isotope Effects in Reaction Rates," Ronald Press Co., New York, N. Y., 1960.

systems, at room temperature. However, the theory shows that under suitable circumstances the total magnitude of the present effect may easily equal (or even greatly exceed) the customary magnitudes of primary isotope effects. In this communication we describe some results of a study using the chemical activation technique in which this expectation is realized.

The *sec*-butyl radical system

$$\mathrm{H} + cis\text{-}\mathrm{CH_3CH{=}CHCH_3} \longrightarrow \mathrm{CH_3\dot{C}HCH_2CH_3}^* \xrightarrow[k_{\epsilon \mathrm{d}_0}]{} \mathrm{CH_3} + \mathrm{C_3H_6}$$

has been well studied.[3] The *sec*-butyl radicals produced at 25° have excess average internal energy, ϵ^+, with respect to the critical energy ϵ_0 for C–C rupture of ~10 kcal./mole, while according to the theory the largest isotope effects should occur when $\epsilon \rightarrow \epsilon_0$, *i.e.*, as $\epsilon^+ \rightarrow 0$. Nonetheless, the butyl radical decomposition still affords the possibility of a very large effect upon replacement of eight hydrogens by deuterium. We have studied the reaction

$$\mathrm{H} + cis\text{-}\mathrm{CD_3CD{=}CDCD_3} \longrightarrow \mathrm{CD_3\dot{C}DCHDCD_3}^* \xrightarrow[k_{\epsilon \mathrm{d}_8}]{} \mathrm{CD_3} + \mathrm{C_3HD_5}$$

at 25° over a range of pressures, p. It has been shown previously[3] that as $p \rightarrow 0$ the apparent experimental average rate constant k_a for decomposition has the form $k_{\mathrm{a}0} = <1/k_\epsilon>^{-1}$, while at limitingly high pressures $k_{\mathrm{a}\infty} = <k_\epsilon>$. We find that the ratio $k_{\mathrm{ad}_0}/k_{\mathrm{ad}_8}$ increases from the value $(k_{\mathrm{ad}_0}/k_{\mathrm{ad}_8})_\infty = 4.0$ to an appreciably larger ratio ($\geqslant 6.0$) for $(k_{\mathrm{ad}_0}/k_{\mathrm{ad}_8})_0$, whose limiting magnitude is unfortunately obscured in this system by experimental error. This variation with pressure may be understood readily, since the average energy of the decomposing radicals, as well as the rate constant k_a, is lower at $p \rightarrow 0$ than it is at $p \rightarrow \infty$; *i.e.*, the average value of ϵ^+ is lower at $p \rightarrow 0$ than at $p \rightarrow \infty$.

Values of the preceding limiting ratios also were calculated according to the accurate quantum statistical treatments previously developed[6] for these chemical activation systems. The numerators and denominators of the above rate constant ratios each have the form of Eq. (1) of reference 6, with the specific collision rate ω set at the limits ∞ and 0, respectively. The radical and activated complex models were quite similar to those previously used, in which all internal rotational and vibrational degrees of freedom were taken as active.[6] Frequencies for the $\mathrm{C_4HD_8}$ system were estimated from the infrared data on $\mathrm{C_3D_6}$[7] and $\mathrm{C_3D_8}$,[8] and were checked with the aid of the Teller–Redlich Product Rule. The ratios calculated for one (non-optimal) set of assumptions are: $p = \infty$, 4.2; and $p = 0$, 5.4. The agreement is quite satisfactory. The present experiments do not give a "pure" secondary effect since the average energy of the $\mathrm{C_4HD_8}$ radicals produced is actually larger than that of the $\mathrm{C_4H_9}$ radicals, *i.e.*, $f(\epsilon)_{\mathrm{d}_8} \neq f(\epsilon)_{\mathrm{d}_0}$[6]; this factor tends to reduce the observed effect, so that the intrinsic isotopic rate ratio at the *same* radical energies is even larger than the values found here.

The present low pressure secondary isotopic ratio is indeed in the conventional range of magnitudes of primary H–D isotope effects at 25°, and the ratios exceed by a factor of ~2 the largest magnitudes previously observed for C–H, C–D secondary intermolecular kinetic isotope effects.[4,9] At −78° the ratios will be even larger.

This study is being extended to other systems and a full account will be given. Part of this work was supported by the Office of Naval Research.

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[5] (a) B. S. Rabinovitch, D. H. Dills, W. H. McLain and J. H. Current, *J. Chem. Phys.*, **32**, 1245 (1960); (b) J. H. Current and B. S. Rabinovitch, to be submitted. These authors describe the magnitude of non-equilibrium primary kinetic isotope effects in related systems of ethyl radicals.

[6] R. E. Harrington, B. S. Rabinovitch and R. W. Diesen, *J. Chem. Phys.*, **32**, 1245 (1960); B. S. Rabinovitch and J. H. Current, *ibid.*, **35**, 2250 (1961).

[7] (a) R. Lord and P. Venkateswarlu, *J. Opt. Soc. Am.*, **43**, 1079 (1953); (b) L. M. Sverdlov, *Prod. Acad. Sci. U.S.S.R.* (Chem. Sect.), **106**, 21 (1956) (Engl. transl.).

[8] H. L. McMurry and V. Thornton, *J. Chem. Phys.*, **19**, 1014 (1951).

[9] K. T. Leffek, J. A. Llewellyn and R. E. Robertson, *Can. J. Chem.* **38**, 2171 (1960); V. J. Shiner, *J. Am. Chem. Soc.*, **75**, 2925 (1953).

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RADICAL AND THERMAL REARRANGEMENT OF ISOPHORONE OXIDE[1]

Sir:

The paucity of intramolecular rearrangements to carbon radicals, as contrasted with the rich and varied lore of carbonium ion rearrangements, has been noted by several authors.[2,3] We now report instances of radical and thermal rearrangements of an α,β-epoxy ketone, which not only supplement the well documented acid and base catalyzed rearrangements of this class of substrates, but represent examples of intramolecular, free radical, acyl group rearrangements.[4,5]

These transformations were first observed with 4-methyl-3,4-epoxy-2-pentanone; however, the tendency of this material to form tars resulted in the use of the less reactive isophorone oxide (I) for detailed investigation. When heated with radical initiators, I was transformed into a mixture of

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[1] This investigation was supported in part by a research grant A-4936 from the National Institutes of Health, Arthritis and Metabolic Diseases Division.

[2] D. J. Cram, "Steric Effects in Organic Chemistry," Edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., Chapter 5, p. 283.

[3] J. A. Berson, C. J. Olsen and J. S. Walia, *J. Am. Chem. Soc.*, **82**, 5000 (1960). References (2) and (7) of this communication constitute a useful record of prior investigations.

[4] D. H. R. Barton, *et al.*, *J. Am. Chem. Soc.*, **83**, 4481 (1961), have reported the photolytic conversion of steroid 11-hydroxy-17-keto nitrite esters to 18-nor-D-homo-$\Delta^{13(17a)}$-11β-hydroxy-17-keto steroids.

[5] Previous reports of thermal rearrangements of α,β-epoxy ketones have not excluded acid catalyzed rearrangement induced by acidic decomposition products, and present no evidence suggesting a radical mechanism: J. Reese, *Ber.*, **75**, 384 (1942); G. V. Pigulevsky and I. K. Mironova, *J. Gen. Chem., U.S.S.R.*, (English translation), **27**, 1184 (1957); H. O. House and R. L. Wasson, *J. Am. Chem. Soc.*, **78**, 4394 (1956).