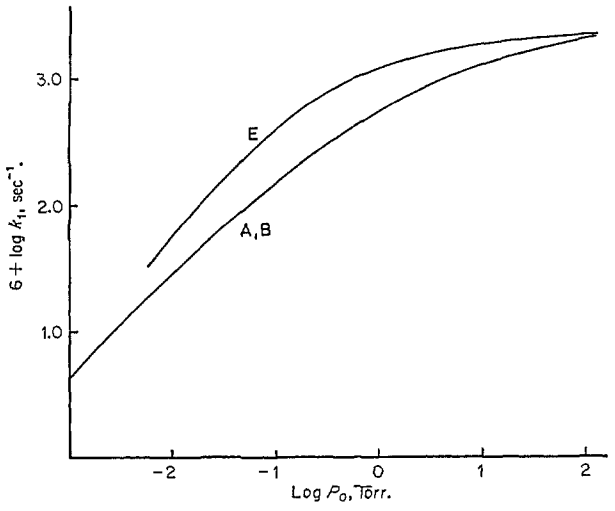


Figure 4. Unimolecular falloff for β-propiolactone at 259°: E = experimental; A, B = RRKM calculated curve for complexes A and B.

The assignment of grouped frequencies to these complexes was made so that the number of vibrational complexions could be calculated by the use of Fowler polynomials.[9] The individual frequencies were based,

complex A complex B

as far as possible, on known vibrational frequencies for a particular bond and thereafter adjustments made to fit the entropy increase of 12.48 cal deg^{-1} mole^{-1}. For the reactant molecule the assignment of Durig[10] was used and included the ring puckering frequency of 113 cm^{-1} instead of the remeasured value of 160 cm^{-1}.[4] The newer value would change the calculation somewhat, making it easier to allow for the large entropy increase.

For complex B it was necessary to introduce two torsional modes of 50 cm^{-1}, the reaction coordinate in both complexes being assumed to be the 1093-cm^{-1} C–O ring stretching model. The grouped frequencies for complex B were thus $(50)^2(200)(300)^2(400)(800)^2(900)(1200)^6(1700)(3000)^4$, and on this basis the entropy of activation was 12.72 cal deg^{-1} mole^{-1}.

In spite of the geometrical form of complex A, it was possible to allow for the large entropy of activation by a reasonable reassignment of frequencies. The ring breathing (1006), stretching (891), and deformation (746 cm^{-1}) had all to be reduced sharply, each to 100 cm^{-1}. This seems not unreasonable for a ring with two very weak bonds. Otherwise, the frequencies of the complex were similar to the stable molecule. An entropy of activation of 12.64 cal deg^{-1} mole^{-1} was calculated with the following frequencies for the complex: $(100)^4(300)^1(500)^1(800)^2(1000)^1(1200)^4(1500)^2(1700)^1(3000)^4$.

It was not possible to make any decision between these two alternatives on the basis of the unimolecular falloff, since for the two complexes an almost identical variation of log (rate constant) − log (initial pressure) curve was obtained. The falloff for both complexes is shown as a single curve (A, B) in Figure 4, along with the experimentally determined curve (E).

To obtain a better correlation with the experimental curve, a reassignment of the frequencies would seem necessary, especially with respect to the reaction coordinate. It is perhaps also necessary to choose a different value for the rate constant for the deactivation of the activated complex, where a bimolecular collision theory value has been used with a collision diameter of 5.3 Å. Especially for complex B, it is unlikely that deactivation and recombination would take place on a simple collision with another molecule.

Acknowledgment. One of us (T. L. J.) is grateful to S. R. C. for the award of a research studentship.

(9) R. H. Fowler, "Statistical Mechanics," 2nd ed, The Macmillan Co., New York, N. Y., 1936.
(10) J. R. Durig, *Spectrochim. Acta*, 19, 1225 (1963).

Communications to the Editor

Kinetic Isotope Effects and CD_3 *vs.* CH_3 Migration

Sir:

In rearrangement reactions in which two or more equivalent methyl groups can migrate, comparison of kinetic isotope effects with the extent of CH_3 *vs.* CD_3 migration would provide a direct means of determining whether or not the step of methyl migration corresponds to the rate-controlling step. For this approach to be practical, it is first necessary to establish whether CH_3 and CD_3 have a sufficiently different migratory aptitude and to experimentally check the theoretical correlation between kinetic isotope effects and extent of CH_3 *vs.* CD_3 migration in a reaction in which the rate-controlling step does correspond to the migration step.

Methyl migration in the rate-controlling step appeared likely for the acid-catalyzed rearrangement of 1,1-diphenyl-2-methyl-1,2-propanediol, reported to yield only the methyl migration product.[1-4] We observed 11–12% phenyl migration as well. Rate plots were linear for at least three half-lives. Data over an

(1) H. Meerwein, *Ann.*, 396, 259 (1913).
(2) W. Parry, *J. Chem. Soc.*, 107, 108 (1915).
(3) M. Ramart-Lucas and F. Salmon-Lagagneur, *Compt. Rend.*, 188, 1301 (1929).
(4) T. Szeki, *Magyar Chem. Lapja*, 1, 25 (1946).

Table I. Isotope Effects in Methyl Rearrangement of 1,1-Diphenyl-2-methylpropane-1,2-diol at 25°[a,b]

Solvent, % H_2SO_4 added to HOAc[c]	No. of runs[d]	$k_I \times 10^4$, sec^{-1} [e]	k_I/k_{III}	k_I/k_{III}	Experimental mass ratios[f] 180	181	182	183	184	185	186
46.26	4	0.959 ± 0.011	1.065	1.149	2.7	133.7	22.1	11.4	100	15.3	1.2
48.75	2	2.204 ± 0.004	1.056		2.5	133.3	22.6	11.7	100	15.3	1.2
49.97	2	2.919 ± 0.032	1.077		2.6	134.3	21.8	11.7	100	15.3	1.2
53.14	2	7.284 ± 0.032	1.057		2.6	130.9	22.3	11.7	100	15.2	1.2
54.75	4	14.35 ± 0.11	1.078	1.204	2.6	134.4	22.6	11.7	100	15.3	1.2
57.37	3	35.71 ± 0.11	1.062		2.7	133.7	22.1	11.4	100	15.3	1.2
58.95	2	55.6 ± 0.45	1.080		3.3	133.5	22.6	11.6	100	15.1	1.2
Aqueous 50.30% H_2SO_4	6	7.185 ± 0.051	1.078	1.177		132.5	24.6	11.7	100	15.9	
			Av 1.071[g] ±0.009[h]	1.177 ±0.019[h]	Av 2.6	133.0	22.8	11.6	100	15.4	1.2

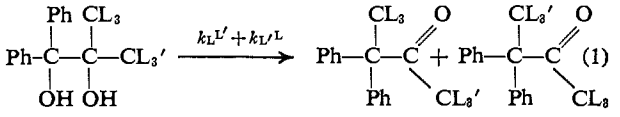
[a] The standard deviation of individual rate constants, calculated by computer, is less than 1%. [b] Rate constants, obtained by following uv changes, are corrected for a small extent phenyl migration. [c] Solvents were prepared by dilution of 20 ml of HOAc to 100 ml with the per cent aqueous H_2SO_4 indicated. [d] Number of individual rate constant determinations on compounds I and II. Three determinations were made on compound III in each instance. [e] Average deviation given. [f] Experimental values, relative to $Ph_2CD_3^+$ (mass 184) = 100, of $Ph_2CCl_3^+$ fragments in the mass spectrum of the product from II. [g] The averages are weighted according to the number of runs. [h] Average deviation of listed values.

Table II. Kinetic Isotope Effects in the Solvolysis of $(CL_3)_3CCHCH_3OBs$[a]

Solvent (temp, °C)	$k_H \times 10^4$, sec^{-1}	$k_D \times 10^{-4}$	k_H/k_D
43.32% EtOH (40)	8.14 ± 0.05[b]	8.32 ± 0.08[b]	0.979 ± 0.017[c]
95% CF_3CO_2H (10.16)	22.1 ± 0.3[d]	22.4 ± 0.3[d]	0.986 ± 0.014[c]

[a] The standard deviation of individual rate constants, calculated by computer, is less than 1%. [b] Average devintion, three runs. [c] Deviation based on opposite extremes in average deviations for k_H and k_D. [d] Average deviation, four runs.

interval of 1.5 to 2 half-lives (15 to 20 points) were used to calculate k_{obsd} values by computer.



(1)

I, $CL_3 = CL_3' = CH_3$
II, $CL_3 = CH_3$; $CL_3' = CD_3$
III, $CL_3 = CL_3' = CD_3$

$$k_I = 2k_H^H$$
$$k_{II} = k_H^D + k_D^H \quad (2)$$
$$k_{III} = 2k_D^D$$

Sample II products,[5] obtained under kinetic conditions, were analyzed mass spectrophotometrically, the count being made at intense peaks corresponding to the fragments $Ph_2CCL_3^+$. Neither the $Ph_2CCL_3^+$ ratios nor the kinetic isotope effects showed a significant trend with solvent (Table I). Consequently, only the average values were used in further calculations. After correction for natural ^{13}C, the ratio of migrated groups $CD_3:CHD_2:CH_2D:CH_3$ is 100:10.2:0.4:135.3. About 10% of the $Ph_2\overset{+}{C}CH_3$ arises from $Ph_2COHCOHCH_3$-CHD_2 and a small amount of $Ph_2COHCOHCH_3CH_2D$.[5] A correction for this was made by assuming that per D in CL_3' the effect on the free energy of activation is additive. The value thus obtained is $k_{CH_3}^{CD_3}/k_{CD_3}^{CH_3}$ = 1.232, the ratio of rate constants for CH_3 *vs.* CD_3 migration in the migration step of II.[6,7] It is the product of an isotope effect in the migrating group and an inverse isotope effect in the nonmigrating group.

The ratio $k_{CH_3}^{CD_3}/k_{CD_3}^{CH_3}$ for compound II is directly a rate constant ratio for the migration step *alone*, whereas k_H^D/k_D^H is the ratio of the kinetic constants as defined in eq 2.[6] The ratios will be equal theoretically if the migration step and rate-controlling step are the same.[8] By setting these ratios equal, and applying eq 2, one can calculate values for all $k_L^{L'}$. For k_H^H/k_D^H, the purely migrational isotope effect with CH_3 as the nonmigrating group, one obtains the value 1.195. The migrational isotope effect with CD_3 as the nonmigrating group, k_H^D/k_D^D, is 1.214. The secondary effects in the nonmigrating group are k_H^H/k_H^D = 0.970 and k_D^H/k_D^D = 0.985. The reasonable agreement between the two migrational isotope effects and the two nonmigrational isotope effects constitutes good evidence that the rate-controlling and migration steps are indeed one and the same.

The migrational isotope effect is reasonably large, indicating an appreciable "loosening" of zero-point vibrations in the migrating methyl, and is consistent with a decrease in electron density within the migrating group. On the other hand, the nonmigrational isotope effect is small and may not differ significantly from unity. In any event, it appears that the positive charge in the activated complex is not greatly shared by the nonmigrating methyl group, due perhaps in part to the conjugative efficiency of the hydroxyl substituent.

The deuterium results do not enable distinction between rate-controlling rearrangement of a benzhydryl carbonium ion (free or "encumbered") or rate-controlling migration synchronous with cleavage of the C–OH_2^+ bond, although the former would appear to be more likely *per se*. Migration after C–OH_2^+ bond cleavage is supported by the finding that in ^{18}O enriched 30%

(5) The sample of II was 96.3 ± 0.5% isotopically pure, and that of III, 95.7 + 0.5%, according to nmr analysis. The small percentage of hydrogen negligibly influences k_{obsd} but requires correction of observed product isotope ratios.

(6) The subscript in $k_{CL_3}^{CL_3'}$ and $k_L^{L'}$ refers to the migrating group; the superscript refers to the nonmigrating group.

(7) The lower limit value is 1.223, based on the same relative migration rates for CHD_2 and CH_2D as for CD_3. The upper limit value is 1.248, based on the same relative migration rates for CHD_2 and CH_2D as for CH_3.

(8) This assumes that rotational equilibrium is established prior to rearrangement.

sulfuric acid at 25° ^{18}O exchange, found only at the benzhydryl oxygen, was 50% complete in 5 min, conditions under which no detectable rearrangement reaction occurs.

The Neopentyl System. The neopentyl system is one that appears *per se* much more likely to involve methyl participation. Table II lists observed rate constants for solvolysis of α-methylneopentyl brosylate and its γ-d_9 derivative (93.7% isotopically pure). There is practically no isotope effect, even in the weakly basic 95% trifluoroacetic acid, which should favor the direct formation of the intrinsically more stable rearranged tertiary carbonium ion.[9,10] Insofar as rate-controlling synchronous methyl migration might be expected to give the same sort of appreciable positive kinetic isotope effect as found above for a rate-controlling nonsynchronous methyl migration, the results would indicate that methyl migration occurs after the rate-controlling step. However, this is yet to be fully determined by a comparison of kinetic isotope effects *and* product ratios, now being carried out on γ-deuterated neopentyl *p*-nitrobenzenesulfonates.

(9) V. J. Shiner, Jr., R. Fisher, and W. Dowd, *J. Am. Chem. Soc.*, 91, 7748 (1969), report $k_H/k_{\gamma\text{-}d_9}$ values very slightly greater than unity in three solvents. On this and other evidence, they have independently concluded that rearrangement follows rate-controlling ion pair formation. We are grateful to Professor Shiner for communication of this work prior to publication.

(10) For solvolysis of γ-deuterated alkyl methanesulfonates in water, Robertson reports k_H/k_D: neopentyl (1.017), isobutyl (0.968), and propyl (0.924).[11]

(11) M. J. Blandmer and R. E. Robertson, *Can. J. Chem.*, 42, 2137 (1964); K. T. Leffek, J. A. Llewellyn, and R. E. Robertson, *J. Am. Chem. Soc.*, 82, 6315 (1960).

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Enhancement of Solvolysis Rates by Wagner–Meerwein Rearrangements of Ion Pairs

Sir:

The detection of a large ratio of ion-pair return to solvolysis for isopropyl cation–brosylate tight ion pairs in trifluoroacetic acid (TFA) at 25°[1] emphasizes the necessity to estimate ionization rates *in the absence of internal return* in order to distinguish between acceleration due to participation in ionization and acceleration due to participation *after* ionization. We wish to propose that 3,3-dimethyl-2-butyl ("pinacolyl") brosylate is a useful reference compound to estimate unassisted ionization rates of secondary brosylates in the absence of return.

t-Butylethylene (0.1 *M*) in trifluoroacetic acid at 12° reacts with *p*-bromobenzenesulfonic acid (HOBs, 0.125 *M*) so rapidly that within 20 sec after mixing the nmr spectrum shows no proton resonances except those due to (rearranged) 2,3-dimethyl-2-butyl trifluoroacetate. No pinacolyl brosylate is detected even though its half-life under these conditions is ~16 sec. *t*-Butylethylene reacts with trifluoroacetic acid at 25° with a first-order rate constant some ten times that of propene; only a few per cent of unrearranged secondary ester is produced. These results are consistent with the pinacolyl cation rearranging to the 2,3-dimethyl-2-butyl cation in the tight ion pair in TFA faster than it combines with the brosylate counterion. Thus, in the trifluoroacetolysis of pinacolyl brosylate the formation of the tight ion pair is rate determining while with isopropyl brosylate the *dissociation* of the tight ion pair is rate determining. This explains why the pinacolyl compound solvolyzes ~2800 times faster than isopropyl brosylate in TFA. This acceleration is not due to participation in ionization since, as reported above, the addition of trifluoroacetic acid to the corresponding alkene is only accelerated by a factor of about 10 as expected from a normal inductive effect. The fact that the products are almost exclusively those of Wagner–Meerwein rearrangement confirms that, as expected, these electrophilic additions involve carbonium ion type intermediates. The deuterium isotope effects for the solvolysis of pinacolyl brosylate in trifluoroethanol–water and ethanol–water solvents (Table I) also indicate that ionization without participation is the rate-determining step.

Table I. Deuterium Effects in Solvolysis of 3,3-Dimethyl-2-butyl Brosylates at 25°[a]

Solvent[b]	$k_H/k_{\alpha\text{-}d}$	$k_H/k_{\beta\text{-}d_3}$	$k_H/k_{\gamma\text{-}d_9}$
97 T	1.153	1.188	1.011
70 T	1.152	1.205	
50 E	1.159	1.205	1.003

[a] From rates determined conductometrically. [b] 97 T is 97% trifluoroethanol–3% water; 50 E is 50 vol % ethanol–50 vol % water, etc.

The α-*d* and β-d_3 effects are not strongly solvent dependent and are both smaller than the limiting values[1,2] of 1.22 and 1.46, consistent with some nucleophilic attachment of the leaving group in the transition state. The γ-d_9 effect is very small, indicating that there is no migration of the methyl group in the rate-determining step.[3]

The smaller isotope effects for isopropyl brosylate solvolysis in TFE–water solvents (Table II) can be

Table II. Solvolysis Rate Constants[a] for Isopropyl ($k_{i\text{-}Pr}$) and 3,3-Dimethyl-2-butyl (k_{Pin}) Brosylates

Solvent[b]	$k_{i\text{-}Pr}$	k_{Pin}	$k_{i\text{-}Pr}/k_{Pin}$	$k_H/k_{i\text{-}P\text{-}\alpha\text{-}d}$
TFA	1.5[c]	4200[d]	0.00036	1.22[e]
97 T	0.1075	7.98	0.026	1.16
70 T	1.41	10.64	0.107	1.140
50 T	1.833	16.56	0.172	1.122
50 E	7.20	10.11	0.714	1.114
80 E	1.447	0.6357	2.27	1.098
90 E	0.636	0.190[f]	3.35	1.083

[a] Units of 10^{-5} sec^{-1} at 25° determined conductometrically. [b] See footnote *b*, Table I. [c] Estimated for 12° by extrapolation from the rate at 25°. [d] Value determined by nmr at 12°. [e] Value at 25° from ref 2. [f] Estimated from a plot of log *k* *vs.* *Y*.

(2) A. Streitwieser, Jr., and G. A. Dafforn, *Tetrahedron Letters*, 1263 (1969).

(3) Professor W. M. Schubert and P. N. LeFevre have also independently observed the absence of a significant γ-d_9 effect in the 50% aqueous ethanolysis and the 95% aqueous trifluoroacetolysis of pinacolyl brosylate and have also interpreted this as indicating the absence of participation in ionization.[4] We are grateful to Professor Schubert for the communication of these results prior to publication.

(4) P. H. LeFevre, Ph.D. Thesis, University of Washington, 1968; W. M. Schubert and P. H. LeFevre, *J. Amer. Chem. Soc.*, 91, 7746 (1969).