[Contribution from the Department of Chemistry, University of California at Los Angeles]

Salt Effects and Ion Pairs in Solvolysis and Related Reactions. III.[1] Common Ion Rate Depression and Exchange of Anions during Acetolysis[2,3]

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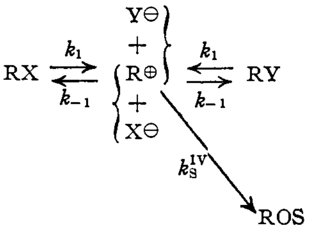
The existence of carbonium ion intermediates as ion pairs as well as dissociated species may modify substantially the kinetics associated with return or exchange reactions accompanying solvolysis of RX. Where common ion returns dissociated carbonium ion to an ion pair which can itself give rise to solvolysis product, there is an upper limit to the amount of rate depression by common ion. One of three limiting situations where common ion rate depression due to external ion return will not be visible during a kinetic run, or as a result of added common ion, involves very efficient external ion return. Therefore, the absence of common ion depression is not decisive, but its presence does indicate at least some external ion return. While external ion return is not a sufficient condition for the appearance of common ion rate depression, it is sufficient for the appearance of exchange involving an ion Y$^\ominus$ similar to X$^\ominus$. The absence of such exchange permits the conclusion that external ion return is absent. However, since exchange can occur at ion pair stages of ionization–dissociation, the presence of exchange is consistent with ionization but it does not require dissociation. In acetolysis, common ion rate depression is absent for *exo*-norbornyl, 1-*p*-anisyl-2-propyl and *dl*-threo-3-anisyl-2-butyl but is visible for cholesteryl and 2-(2,4-dimethoxyphenyl)-ethyl toluenesulfonates or bromobenzenesulfonates. Toluenesulfonate–bromobenzenesulfonate exchange does not accompany acetolysis in the case of *exo*-norbornyl but occurs efficiently with the 3-anisyl-2-butyl, cholesteryl and 2,4-dimethoxyphenylethyl systems. These results show that external ion return does not occur in acetolysis of norbornyl but does occur with cholesteryl and 2,4-dimethoxyphenylethyl arylsulfonates. By considering the spectrum of systems, it is possible to conclude that dissociated carbonium ion is not formed during acetolysis of the 3-anisyl-2-butyl, 1-anisyl-2-propyl and *exo*-norbornyl arylsulfonates. On this basis, the exchange reaction accompanying acetolysis of 3-anisyl-2-butyl bromobenzenesulfonate involves ion pairs but not dissociated carbonium ions.

Introduction.—The dissociated form of the carbonium ion intermediate, R$^\oplus$, is often employed in the interpretation of solvolysis of materials, RX, such as alkyl halides and benzenesulfonates. A classic pertinent example is the hydrolysis of benzhydryl halides in aqueous acetone, interpreted by Hughes, Ingold and co-workers[4] with the reaction scheme in equation 1. In this scheme, return of the carbonium ion to the covalent condition by common ion, X$^\ominus$, is associated with an accompanying depression of the rate of formation of solvolysis product, ROS, termed "mass-law depression" by Hughes and Ingold.[4] These investigators fitted the depression of solvolysis rate by accumulating or added common ion with equation 2. In this reaction scheme, the first order rate of solvolysis



(1)

$$\frac{-\text{d(RX)}}{}\ (\text{RX}) = k_1\left[\frac{k_s^{IV}}{k_s^{IV} + k_{-1}(\text{X}^\ominus)}\right] = k_1\left[\frac{1}{1 + \alpha(\text{X}^\ominus)}\right] \qquad (2)$$

$$\alpha = k_{-1}/k_s^{IV}$$

approaches zero as the common ion concentration increases.

The inclusion of a non-common ion, Y$^\ominus$, in the solvolysis solution permits Y$^\ominus$ to compete for the intermediate R$^\oplus$. This gives rise to an exchange reaction which produces RY. The exchange reaction was treated[4] with the aid of an α, or k_{-1}/k_s^{IV} ratio, applicable to Y$^\ominus$ instead of X$^\ominus$. This same α is applicable to common ion rate depression in solvolysis of RY.

The simple kinetic scheme in equations 1 and 2 becomes inadequate for many systems under many of the conditions employed in organic chemistry. This paper deals with common ion rate depression and exchange in acetolysis of certain toluenesulfonates and bromobenzenesulfonates. These are part of a group of substances which have been useful in the elucidation of the intimate mechanism of solvolysis and related reactions. The various studies are described in a series of papers to which this is introductory.

Ion Pairs.—A necessary elaboration of the kinetic scheme of equations 1 and 2, under some conditions at least, is explicit recognition of an ion pair form as well as the dissociated form of the carbonium ion. For example, the ion pair is important for internal return,[5] mechanism and stereochemistry of solvolysis[5,6] and conductivity of solutions of triarylmethyl chlorides.[7]

For some phenomena,[1] it is necessary to consider more than one ion pair stage in the whole process of ionization and dissociation leading from RX to R$^\oplus$. While this is not so essential for the immediate purposes of the present paper, it is convenient to base the present discussion on a kinetic scheme as elaborate as is necessary in later papers of the series. In this way, over-all economy of kinetic derivations for the whole series of papers can be achieved, and the present paper can more

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[1] Previous papers in this series: (a) I, S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, This Journal, **76**, 2597 (1954); (b) II, S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, *Chemistry and Industry*, 664 (1954).

[2] Research sponsored by the Office of Ordnance Research, U. S. Army.

[3] Supported in part by the Office of Naval Research.

[4] L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

[5] (a) W. G. Young, S. Winstein and H. Goering, This Journal, **73**, 1958 (1951); (b) S. Winstein, E. Grunwald and H. W. Jones, *ibid.*, **73**, 2700 (1951); (c) S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952); (d) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952).

[6] (a) S. Winstein and R. E. Buckles, *ibid.*, **64**, 2780 (1942); (b) C. G. Swain, *ibid.*, **70**, 1119 (1948); (c) W. Doering and H. H. Zeiss, *ibid.*, **75**, 4733 (1953).

[7] *E.g.*, A. G. Evans, *et al.*, *Trans. Faraday Soc.*, **47**, 711 (1951); **50**, 16 (1954).

efficiently serve as an introduction to the series. The ion pair postulated in the internal return phenomenon was the intimate or internal variety II, two ions of opposite charge in contact, with no solvent molecules interposted between them. Further separation of the two ions and interposition of a small number of solvent molecules between them gives rise to the solvent-separated or external ion pair[8] III. Similarly, bringing dissociated carbonium ion IV and $X^\ominus$ together in a solvent of low dielectric constant would also give rise to III, the usually depicted pair of solvated ions held together by coulombic attraction. Therefore, external or solvent-separated ion pair III intervenes between the intimate ion pair II and the dissociated ion IV. On this basis, three varieties of carbonium ion, II, III, and IV, representing progressively further stages of ionization–dissociation, will be employed in the formulation of acetolysis.[1]

The furthest stage of ionization–dissociation which is reached in any reaction involving ionization of RX may vary. Solvolysis product may arise from more than one of the varieties of carbonium ion; the rate of the product-forming reaction of an ionic intermediate II or III may exceed the rate of progression to the next stage in the ionization–dissociation process. The scheme shown in equation 4 is designed for a case where ROS arises from solvent-separated ion pair

$$\mathrm{I} \xrightarrow{\text{ionization}} \mathrm{II} \qquad \mathrm{III} \xrightarrow{\text{dissociation}} \mathrm{IV} \qquad (3)$$

intimate or internal ion pair — external or solvent-separated ion pair — dissociated ions

$$\begin{tikzcd}
RX \arrow[r, shift left, "k_1"] & R^\oplus X^\ominus \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] & R^\oplus \| X^\ominus \arrow[l, shift left, "k_{-2}"] \arrow[r, shift left, "k_3"] \arrow[d, "k_s^{III}"] & R^\oplus + X^\ominus \arrow[l, shift left, "k_{-3}"] \arrow[d, "k_s^{IV}"] & (4) \\
 & & ROS & ROS &
\end{tikzcd}$$

III and dissociated ion IV, with rate constants k_s^{III} and k_s^{IV}, respectively.[1] This must not be misunderstood[9] as an indication that we believe the intimate ion pair II does not ever give rise to ROS. As we have indicated previously, the intimate ion pair II is thought to be able to give rise to ROS in solvolysis of α,α-dimethylallyl chloride,[5a] *trans*-2-acetoxycyclohexyl *p*-toluenesulfonate[10] and *t*-butyl chloride.[5b]

Return.—Return to covalent RX accompanying solvolysis may be from any one of the ionic stages, II, III or IV, as the furthest stage of ionization–dissociation. In speaking of return to RX accompanying solvolysis, the following terminology is suggested.

(i) "internal return," return from internal ion pair II
(ii) "ion pair return," return from ion pairs II and/or III
(iii) "external ion pair return," return from external ion pair III
(iv) "external return," return from III and/or IV
(v) "external ion return," return from IV

Just as return may involve various varieties of carbonium ion, exchange may involve not only the dissociated carbonium ion IV, but also ion pairs.

Common ion rate depression and exchange often have been employed as diagnostic tools in seeking information on the intimate mechanism of carbonium ion reactions such as substitution and rearrangement. Thus, the absence of common ion rate depression often has been taken as proof of the absence of external ion return. Also, exchange has sometimes been taken as evidence for dissociation.

Theory of Common Ion Rate Depression.—For the solvolysis scheme in equation 4, k_t, the first-order titrimetric solvolysis rate constant, may be defined by equation 5, where d(ROS)/d*t* is the rate of formation of solvolyis product and (RX) is the

$$k_t = \frac{d(\mathrm{ROS})}{dt} \Big/ (\mathrm{RX}) \qquad (5)$$

concentration of solvolyzing material RX. In terms of rate constants defined by equation 4, k_t is given by equation 6 (see Kinetic Appendix).

$$k_t = k_1 \Big/ 1 + \frac{(k_{-1}/k_2)}{\left[k_s^{III} + \dfrac{k_3 k_s^{IV}}{k_{-3}(X^\ominus) + k_s^{IV}}\right] \Big/ \left[k_{-2} + k_s^{III} + \dfrac{k_3 k_s^{IV}}{k_{-3}(X^\ominus) + k_s^{IV}}\right]} \qquad (6)$$

The depression of rate by common ion is accounted for by the term involving $k_{-3}(X^\ominus)$ which modifies k_3 in equation 6.

Where common ion $X^\ominus$ returns dissociated carbonium ion $R^\oplus$ to an ion pair which can itself give rise to solvolysis product, we can anticipate an upper limit to the amount of rate depression by common ion. This is in contrast with the simpler situation depicted in equations 1 and 2, where, in principle, except for practical considerations of maximum possible concentration of $X^\ominus$, there is no limit. The maximum amount of rate depression by common ion predicted by equation 6 can be gaged easily as follows: The undepressed rate constant k_t^0 when $k_{-3}(X^\ominus)$ is zero will be given by equation 7. The fully depressed rate constant, k_t^d, when $k_{-3}(X^\ominus) \gg k_s^{IV}$ or, in other words, $R^\oplus$ is

$$k_t^0 = k_1 \Big/ 1 + \frac{(k_{-1}/k_2)}{(k_s^{III} + k_3)/(k_{-2} + k_s^{III} + k_3)} \qquad (7)$$

being all returned to $R^\oplus \| X^\ominus$, will be given by equation 8.

$$k_t^d = k_1 \Big/ 1 + \frac{(k_{-1}/k_2)}{k_s^{III}/(k_{-2} + k_s^{III})} \qquad (8)$$

Where there is external ion pair return,[11] there will be three limiting situations where common ion rate depression due to external ion return will not be visible during a kinetic run or as a result of added common ion

(i) $k_s^{III} \gg k_3$; dissociated carbonium ion IV is not formed; in this case k_t is given by equation 8
(ii) $k_s^{IV} \gg k_{-3}(X^-)$; IV is formed but is not returned; in this case k_t is given by equation 7
(iii) $k_{-3}(X^-) \gg k_s^{IV}$ throughout the observed kinetic run; return of IV to III is essentially complete; ROS arises essentially entirely from III; in this case k_t has the fully depressed value given by equation 8

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[8] The term "solvent-separated," was suggested to one of us (S.W.) by E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954).

[9] See R. F. Hudson and B. Saville, *Chemistry and Industry*, 1423 (1954).

[10] S. Winstein and R. Heck, THIS JOURNAL, **74**, 5584 (1952).

[11] If there is no return from III, in other words, $k_s^{III} \gg k_{-2}$, no common ion rate depression is expected; for $k_s^{III} \gg k_{-2}$, equation 6 degenerates to $k_t = k_1/[1 + (k_1/k_2)]$.

One of the limiting situations, namely (iii), involves very efficient external ion return and yet no visible common ion depression.

As is summarized in Table I, the lack of common ion rate depression is not by itself evidence against dissociation and return from IV. While external ion return is a necessary condition for the appearance of common ion rate depression, it is not a sufficient condition. Although the absence of common ion rate depression is not decisive, its presence is unambiguous, indicating at least some external ion return.

TABLE I

CONNECTION BETWEEN RETURN, COMMON ION RATE DEPRESSION AND EXCHANGE

	Possible combinations of:	
Return from	Common ion depression	Exchange
Ion pairs	No	No (a)
	No	Yes (b)
Dissociated ions	Yes	Yes (c)
	No	Yes (d)

While external ion return is not a sufficient condition for the appearance of common ion rate depression, it is sufficient for the appearance of exchange involving an ion $Y^{\ominus}$ similar to $X^{\ominus}$. This is indicated in Table I. However, exchange can occur at ion pair stages so occurrence of exchange does not furnish an unambiguous answer regarding external ion return. The presence of exchange is consistent with ionization but it does not require dissociation. The absence of exchange does, however, permit the definite conclusion that external ion return is absent (Table I).

Common Ion Rate Depression.—The compounds whose acetolysis has been surveyed for the presence or absence of common ion rate depression, as summarized in Table II, are *exo*-norbornyl,[5c,12] 1-*p*-anisyl-2-propyl,[13] *dl-threo*-3-*p*-anisyl-2-butyl,[13a,14] cholesteryl[15] and 2-(2,4-dimethoxy-phenyl)-ethyl[16] toluenesulfonates or *p*-bromobenzenesulfonates. All of these substances undergo acetolysis by way of anchimerically assisted ionization to bridged carbonium ions.

In the case of the first four compounds in Table II, no indication of a downward drift in rate constant, k_t, was evident in acetolysis of 0.01–0.03 *M* solutions. Solvolyses were followed from *ca.* 5 to 90% of completion. For *exo*-norbornyl *p*-bromobenzenesulfonate[12] and 1-*p*-anisyl-2-propyl *p*-toluenesulfonate[13a] the present observations were consistent with previous work. For *dl-threo*-3-*p*-anisyl-2-butyl *p*-bromobenzenesulfonate, a sample run is illustrated in Table III. Since medium effects due to accumulating toluenesulfonic or bromobenzenesulfonic acid are very small as demonstrated in other work,[17] the absence of a downward drift in k_t during a run is essentially synonymous with absence of common ion rate depression during such a run.

TABLE II

COMMON ION SALT EFFECTS ON RATES OF ACETOLYSIS

Compound	Temp., °C.	Concn. 10^2 *M*	Other solute	Concn. 10^2 *M*	k, sec.$^{-1}$
exo-Norbornyl OBs	25.0	3.02			$(8.95 \pm 0.07) \times 10^{-5}$
	25.0	1.45			$(9.25 \pm .13) \times 10^{-5}$
	25.0	3.02	LiOBs	2.50	$(1.00 \pm .03) \times 10^{-4}$
1-*p*-Anisyl-2-propyl OTs	50.0	3.21			$(1.198 \pm .007) \times 10^{-5}$
dl-threo-3-*p*-Anisyl-2-butyl OBs	25.0	1.00			$(1.96 \pm .03) \times 10^{-5}$
	25.0	1.00	LiOBs	1.01	$(2.05 \pm .04) \times 10^{-5}$
dl-threo-3-*p*-Anisyl-2-butyl OTs	25.0	1.05			$(5.77 \pm .10) \times 10^{-6}$
	25.0	1.10	LiOTs	1.00	$(5.75 \pm .24) \times 10^{-6}$
Cholesteryl OTs	50.0	0.545			$(1.30 \pm .02) \times 10^{-4}$
	50.0	.545			$(1.30 \pm .01) \times 10^{-4}$
	50.0	.545	LiOTs	1.00	$(1.10 \pm .05) \times 10^{-4}$
	50.0	.545	LiOTs	3.00	$(1.14 \pm .07) \times 10^{-4}$
	50.0	.545	LiOTs	6.00	$(1.20 \pm .06) \times 10^{-4}$
Cholesteryl OBs	50.0	.552			$(4.51 \pm .10) \times 10^{-4}$
	50.0	.552	LiOBs	1.00	$(4.27 \pm .07) \times 10^{-4}$
	50.0	.552	LiOBs	1.00	$(4.40 \pm .14) \times 10^{-4}$
	50.0	.552	LiOBs	3.00	$(5.04 \pm .05) \times 10^{-4}$
	50.0	.552	LiOBs	3.00	$(5.01 \pm .08) \times 10^{-4}$
	50.0	.487	LiOBs	6.00	$(6.06 \pm .18) \times 10^{-4}$
2-(2,4-Dimethoxyphenyl)-ethyl OBs	50.0	1.00			$(4.45 - 3.71)^a \times 10^{-5}$
	50.0	1.00			$(4.62 - 4.13)^b \times 10^{-5}$
	50.0	1.00	LiOBs	1.00	$(3.26 \pm 0.02) \times 10^{-5}$
	50.0	1.00	LiOBs	1.00	$(3.26 \pm .02) \times 10^{-5}$
	50.0	1.00	LiOBs	3.00	$(3.59 \pm .10) \times 10^{-5}$

[a] 4–81% reaction range; extrapolated initial $k = 4.70 \times 10^{-5}$. [b] 4–49% reaction range; extrapolated initial $k = 4.70 \times 10^{-5}$.

The addition of the appropriate lithium arylsulfonate to the acetolysis solutions for *exo*-nor-

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[12] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, THIS JOURNAL, **74**, 1127 (1952).

[13] (a) S. Winstein, M. Brown, K. C. Schrieber and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952); (b) A. H. Fainberg, unpublished work.

[14] G. C. Robinson, unpublished work.

[15] S. Winstein and R. Adams, THIS JOURNAL, **70**, 838 (1948).

[16] R. Heck, Dissertation, University of California at Los Angeles, 1954.

[17] A. H. Fainberg, unpublished work.

TABLE III

ACETOLYSIS OF 0.00997 *M* *dl-threo*-3-ANISYL-2-BUTYL *p*-BROMOBENZENESULFONATE AT 25.00°

Time, hr.	0.0454 *M* NaOAc per aliquot, ml.	10^6k, sec.$^{-1}$
0	0.010	..
1.00	.082	1.91
3.37	.243	2.00
5.37	.347	1.93
8.37	.499	2.00
12.37	.640	1.96
25.03	.902	1.93
36.28	1.010	2.00
∞	1.092	
	Mean	1.96 ± 0.03

bornyl bromobenzenesulfonate and *dl-threo*-3-anisyl-2-butyl toluenesulfonate and bromobenzenesulfonate also yielded no evidence of common ion rate depression. The rate constant tended to be increased several per cent by *ca.* 0.01 *M* lithium bromobenzenesulfonate, an amount in line with observed medium effects in control cases.[17]

In acetolysis of *ca.* 0.005 *M* solutions of the slowly soluble cholesteryl toluenesulfonate,[15] no evidence of drift in a run was observed (Table II). Inclusion of 0.01 *M* lithium toluenesulfonate depressed the rate constant at 50° from 1.30×10^{-4} to 1.10×10^{-4} sec.$^{-1}$. Further increase in concentration of added lithium toluenesulfonate to 0.03 and 0.06 *M* now caused successive slight increases in k_t above the 1.10×10^{-4} sec.$^{-1}$ figure. Cholesteryl *p*-bromobenzenesulfonate behaved analogously toward addition of lithium *p*-bromobenzenesulfonate except that the later increases in rate constant were larger than in the former case.

The last compound in Table II, 2-(2,4-dimethoxyphenyl)-ethyl bromobenzenesulfonate, was the only one which displayed a downward drifting[16] first-order solvolysis constant during a run (Table II). Table IV summarizes an acetolysis of 0.01 *M* material, instantaneous first-order rate constants, graphically obtained, decreasing from 47×10^{-6} sec.$^{-1}$ and apparently tending to level off at 31×10^{-6} sec.$^{-1}$. This tendency for the rate constant to level off is clearer in acetolysis of 0.03 *M* material as illustrated in Table V. In such a run, fairly steady integrated first-order constants are obtained if they are calculated after *ca.* 40% reaction. When 0.01 *M* lithium bromobenzenesulfonate was added, a steady first-order rate constant was obtained, the value of 32.6×10^{-6} sec.$^{-1}$ being practically equal to the final figure observed without inclusion of salt. Increase of lithium bromobenzenesulfonate concentration to 0.03 *M* produced a small increase in rate constant to 35.9×10^{-6} sec.$^{-1}$, the new value being steady.

TABLE IV

ACETOLYSIS OF 0.0100 *M* 2-(2,4-DIMETHOXYPHENYL)-ETHYL OBs AT 50.0°

Reacn., %	Instant. 10^6k, sec.$^{-1}$	Reacn., %	Instant. 10^6k, sec.$^{-1}$
4	47	62	35
18	44	68	33.5
33	42.5	74	31
47	39.5	81	31

TABLE V

ACETOLYSIS OF 0.0315 *M* 2-(2,4-DIMETHOXYPHENYL)-ETHYL *p*-BROMOBENZENESULFONATE AT 75.00°

Time, sec.	NaOAc soln. per aliquot, ml.	Integrated 10^4k, sec.$^{-1}$	
0	0.455	..	
240	1.090	6.40	
480	1.583	6.10	
780	2.149	6.15	..
1080	2.560	5.93	5.39
1380	2.940	5.93	5.63
1680	3.235	5.84	5.58
1980	3.490	5.79	5.57
2340	3.755	5.78	5.61
∞	4.905		
		Mean	5.56 ± 0.06

The presence or absence of common ion rate depression is summarized in Table VI. With the last three compounds some common ion rate depression is observed either due to common ion salt addition or due to accumulating arylsulfonic acid during a solvolysis run. In all three cases, a minimum solvolysis rate is reached at relatively low concentrations of added lithium arylsulfonate or accumulating arylsulfonic acid. Thus there appears to be an upper limit to the amount of common ion rate depression, bearing out the expectations based on equations 6, 7 and 8.

TABLE VI

OCCURRENCE OF COMMON ION RATE DEPRESSION AND EXCHANGE IN ACETOLYSIS OF VARIOUS ARYLSULFONATES

	Occurrence of:	
Compound	Common ion depression	Exchange
exo-Norbornyl OBs	No	No
$CH_3CH(C_6H_4OCH_3\text{-}p)CH_2OTs$	No	
dl-threo-$CH_3CH(C_6H_4OCH_3\text{-}p)CH(OBs)\text{-}CH_3$	No	Yes
dl-threo-$CH_3CH(C_6H_4OCH_3\text{-}p)CH(OTs)\text{-}CH_3$	No	
Cholesteryl OBs	Yes[a]	Yes
Cholesteryl OTs	Yes[b]	Yes
$2,4\text{-}(CH_3O)_2C_6H_3CH_2CH_2OBs$	Yes[c]	Yes

[a] $k_t^\circ/k_t^d = 1.13$. [b] $k^\circ/k_t^d = 1.20$. [c] $k_t^0/k_t^d = 1.57$.

After the solvolysis rate constant reaches the minimum value, it is actually increased by further addition of common ion salt. This increase is ascribed to acceleration of solvolysis rate by "normal salt effects" which have been neglected so far in the discussion of common ion rate depression. In Fig. 1 are given plots of k_t *vs.* common ion salt concentration for the cholesteryl and dimethoxyphenylethyl arylsulfonates. In two of the cases, the data are sufficient to show that the increase tends to be linear in salt concentration. As other work[1,17] shows, such shallow linear variation of rate with salt concentration is part of the pattern of "normal salt effects" in glacial acetic acid solvent. Extrapolation of the plots in Fig. 1 back to zero salt concentration furnishes estimates of fully depressed solvolysis rate constants, k_t^d, corrected for normal salt effects. These are employed in Table VI to characterize the amount

TABLE VII

SOME NON-COMMON ION SALT EFFECTS ON KINETICS OF ACETOLYSIS

Compound	Temp., °C.	Concn. 10^2 *M*	Other solute	Concn. 10^2 *M*	Reaction range, %	Integ. *k*, sec.$^{-1}$
exo-Norbornyl OBs	25.0	3.02	LiOTs	2.50	10–91	$(9.8 \pm 0.3) \times 10^{-5}$
dl-threo-3-Anisyl-2-butyl OBs	25.0	1.01	LiOTs	1.00	8–89	$(1.61 - 1.42) \times 10^{-5}$
	25.0	1.02	LiOTs	3.00	0–73	$(1.97 - 0.86) \times 10^{-5}$
Cholesteryl OTs	50.0	0.545	LiOBs	6.00	12–92	$(2.56 - 3.18) \times 10^{-4}$
	50.0	.545	LiOBs	6.00	5–85[a]	$(1.58 - 3.34) \times 10^{-4}$
Cholesteryl OBs	50.0	.552	LiOTs	3.00	12–76	$(2.63 - 1.62) \times 10^{-4}$
	50.0	.552	LiOTs	6.00	15–80	$(2.41 - 1.53) \times 10^{-4}$
2-(2,4-Dimethoxyphenyl)-ethyl OBs	50.0	1.00	LiOTs	3.00	1–65	$(3.51 - 1.40) \times 10^{-5}$

[a] Over the range of 46–85%, $k = (3.82 \pm 0.13) \times 10^{-4}$ sec.$^{-1}$.

of common ion rate depression with the ratio, k_t°/k_t^d.

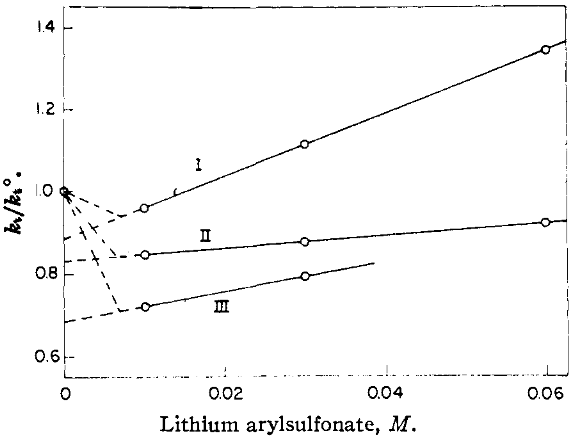

Fig. 1.—Plot of k_t/k_t° *vs.* concentration of lithium arylsulfonate for: I, cholesterylOBs; II, cholesterylOTs; III, 2,4-dimethoxyphenylethylOBs.

Exchange.—Since toluenesulfonates are less reactive than bromobenzenesulfonates by a factor of *ca.* 3, downward drift in observed first-order solvolysis rate constant is a sensitive criterion for exchange of toluenesulfonate ion for bromobenzenesulfonate during acetolysis. In Table VII are summarized the results of acetolysis rate measurements involving addition of non-common ion lithium arylsulfonate to the solvolysis solution.

With *exo*-norbornyl bromobenzenesulfonate, acetolysis in the presence of 0.025 *M* lithium toluenesulfonate proceeded with a rate constant *ca.* 8% higher than without added salt due to a small normal salt effect. No detectable drift in rate constant was in evidence, exchange being entirely negligible.

Even though acetolysis rates of the *threo*-3-anisyl-2-butyl esters were not depressed by common ion salts, inclusion of lithium toluenesulfonate with the bromobenzenesulfonate caused the first-order rate constant to drift down steadily from an initial value near that of bromobenzenesulfonate. This is illustrated in Table VIII and Fig. 2, where it is clear that the instantaneous rate constant approaches that of the toluenesulfonate well along in a run containing 0.03 *M* lithium toluenesulfonate. Thus, exchange of toluenesulfonate for bromobenzenesulfonate is relatively efficient during acetolysis.

The exchange reactions were also relatively efficient in acetolysis of the cholesteryl esters. In acetolysis of bromobenzenesulfonate in the presence of 0.03 or 0.06 *M* lithium toluenesulfonate, formation of toluenesulfonate was rapid and well-nigh complete, judging by the behavior of the first-order solvolysis rate constants. For example, the instantaneous rate constant after 59% reaction in the run with 0.03 *M* lithium toluenesulfonate was fairly steady at 1.20×10^{-4} sec.$^{-1}$, essentially equal to the value of $(1.14 \pm 0.07) \times 10^{-4}$ sec.$^{-1}$

TABLE VIII

ACETOLYSIS OF 0.0102 *M* *dl-threo*-3-ANISYL-2-BUTYL *p*-BROMOBENZENESULFONATE AT 25.00° IN AcOH, 0.0300 *M* IN LiOTs

Time, 10^{-4} sec.	0.0454 *M* NaOAc per aliquot, ml.	$10^5 k_t$, sec.$^{-1}$ Integ.	Instant.
0.0	0.000		1.72
.432	.091	1.97	
.500			1.64
1.000			1.52
1.080	.188	1.71	
2.000			1.39
2.300	.310	1.42	
3.000			1.22
3.240	.431	1.51	
4.000			1.05
4.320	.482	1.31	
5.000			0.92
7.000			0.72
7.841	0.652	1.12	
16.70	.853	0.86	
∞	1.117		

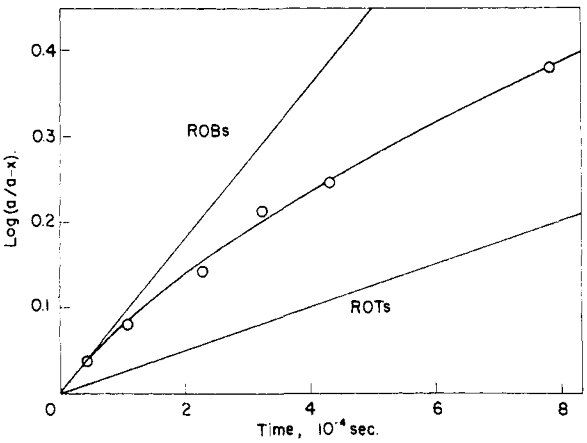

Fig. 2.—Acetolysis at 25.0° of DL-*threo*-3-anisyl-2-butyl *p*-bromobenzenesulfonate with 0.0300 *M* LiOTs.

observed for cholesteryl toluenesulfonate in the presence of 0.03 *M* lithium toluenesulfonate.

In acetolysis of cholesteryl toluenesulfonate in the presence of 0.06 *M* lithium bromobenzenesulfonate, the solvolysis rate constant rises from *ca.* 1.5×10^{-4} sec.$^{-1}$, near the value to be expected for toluenesulfonate, to *ca.* 3.6 to 3.8×10^{-4} sec.$^{-1}$ at 50% acetolysis, where it remains quite constant. This behavior is illustrated graphically in Fig. 3, which compares a first-order plot for the solvolysis exchange with first-order plots for cholesteryl toluenesulfonate in the presence of 0.06 *M* LiOTs and for cholesteryl bromobenzenesulfonate in the presence of 0.06 *M* LiOBs. Apparently, exchange of bromobenzenesulfonate for toluenesulfonate is rapid but only approximately three-fourths complete when an approximate steady-state composition of arylsulfonates is established.[18]

In acetolysis of 2,4-dimethoxyphenylethyl bromobenzenesulfonate in the presence of 0.03 *M* lithium toluenesulfonate, the graphically derived first-order solvolysis rate constant was 3.3×10^{-5} sec.$^{-1}$ initially, and 1.1×10^{-5} sec.$^{-1}$ at only 65% reaction. These data indicate quite rapid and nearly complete conversion of residual arylsulfonate to toluenesulfonate, since the latter rate constant is quite close to the rough figure estimated for toluenesulfonate in the presence of lithium toluenesulfonate, namely, one-third of 3.6×10^{-5} or 1.2×10^{-5} sec.$^{-1}$. The observations on exchange are summarized in Table VI.

Conclusions Regarding Dissociated Carbonium Ions.—As is evident from Table VI, three of the four possible combinations of incidence of common ion rate depression and arylsulfonate exchange, namely a, b, and c of Table I, have been encountered in the present work. With regard to the occurrence of external ion return during acetolysis, the observations give an unambiguous answer for the norbornyl, cholesteryl and dimethoxyphenylethyl derivatives. That such return is negligible for the norbornyl ester is shown by the lack of exchange with toluenesulfonate ion. That at least some external ion return accompanies acetolysis of the cholesteryl and dimethoxyphenylethyl esters under certain conditions is clear from the common ion rate depression. For acetolysis of the 3-anisyl-2-butyl derivative, the present results alone are still ambiguous with regard to external ion return. In this case, no common ion depression is observed but exchange occurs, and it is not at first obvious whether we have here an example of b or d in Table I.

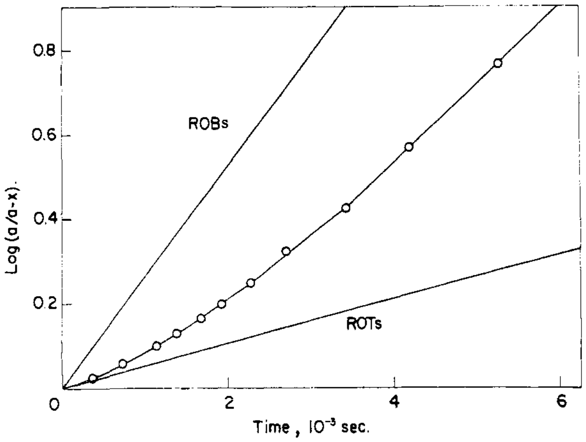

Fig. 3.—Acetolysis of cholesteryl *p*-toluenesulfonate with 0.0600 *M* LiOBs.

It is possible, by considering the spectrum of systems summarized in Table VI, to make common ion rate depression a less ambiguous criterion for external ion return. In Table VI, the compounds are arranged roughly in the order of increasing carbonium ion stability and lifetime, using as a guide the efficiency of capture of carbonium ions by added anions, in highly ionizing solvents as well as acetic acid.[19] It is assumed from previous work[4] that this efficiency increases with carbonium ion stability and lifetime.

Now, the last three compounds in Table VI do show depression of rate by accumulating or added common ion. For these systems, $k_{-3}(\mathrm{X}^{\ominus})/k_{\mathrm{s}}^{\mathrm{IV}}$ is sufficiently large to cause external ion return but not large enough to cause total return very early in the run. We would expect $k_{-3}(\mathrm{X}^{\ominus})/k_{\mathrm{s}}^{\mathrm{IV}}$ to decrease as carbonium ion stability decreases due to increased $k_{\mathrm{s}}^{\mathrm{IV}}$. Therefore, the lack of common ion depression with 3-anisyl-2-butyl esters cannot be due to total external ion return. On this basis, 3-anisyl-2-butyl acetolysis is an example of b and not d (Table I); external ion return is not occurring in acetolysis of this system.

Having eliminated possibility iii for the lack of common ion rate depression in acetolysis of the 3-anisyl-2-butyl system, the remaining possibilities

$$k_{\mathrm{s}}^{\mathrm{IV}}/k_{-3}(\mathrm{X}\ominus) \gg k_{\mathrm{s}}^{\mathrm{III}}/k_3 \tag{10}$$

$$k_{\mathrm{s}}^{\mathrm{IV}}/k_{\mathrm{s}}^{\mathrm{III}} \gg k_{-3}(\mathrm{X}\ominus)/k_3 \tag{11}$$

$$k_{\mathrm{s}}^{\mathrm{IV}}/k_{\mathrm{s}}^{\mathrm{III}} \gg (\mathrm{X}\ominus)/K \tag{12}$$

$$\mathrm{R}\oplus \| \mathrm{X}\ominus \overset{K}{=\!=\!=} \mathrm{R}\oplus + \mathrm{X}\ominus \tag{13}$$

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[18] The conversion of cholesteryl bromobenzenesulfonate to toluenesulfonate is more complete in the exchange experiments than the reverse conversion of toluenesulfonate to bromobenzenesulfonate. Even if the competitive behavior of the various carbonium ion species is identical for solvolysis of both the bromobenzenesulfonate and toluenesulfonate, the more complete exchange in one direction than the other is to be expected. This follows from the lower ionization rate of the toluenesulfonate relative to the bromobenzenesulfonate. The argument may be based on the simplified reaction scheme

$$\begin{tikzcd}
\mathrm{ROBs} \arrow[r, shift left, "3(\mathrm{LiOTs})"] \arrow[d] & \mathrm{ROTs} \arrow[l, shift left, "(\mathrm{LiOBs})"] \arrow[d] \\
\mathrm{ROS} & \mathrm{ROS}
\end{tikzcd}$$

which has ROTs going to ROBs with a relative rate constant proportional to (LiOBs), but ROBs going to ROTs with a relative rate constant proportional to 3(LiOTs) to allow for threefold greater ionization rate of the bromobenzenesulfonate. With exchange considerably faster than solvolysis, the composition of unsolvolyzed arylsulfonates soon reaches and is maintained at a value given by equation 9. When

$$\frac{(\mathrm{ROTs})}{(\mathrm{ROBs})} = \frac{3(\mathrm{LiOTs})}{(\mathrm{LiOBs})} \tag{9}$$

the molarity of added non-common arylsulfonate salt is ten times the concentration of arylsulfonate ion being produced, the ratio (ROTs)/(ROBs) will reach *ca.* 30 in the conversion of bromobenzenesulfonate to toluenesulfonate. However, the ratio (ROBs)/(ROTs) reaches only *ca.* 3 in the conversion of toluenesulfonate to bromobenzenesulfonate.

[19] E. Clippinger, unpublished work.

are (i) dissociation does not occur; (ii) dissociation occurs but $k_s^{IV}/k_{-3}(X^\ominus)$ is very large. Examining (ii) we see that it requires k_s^{III}/k_3 to be small (and $k_s^{IV}/k_{-3}(X^\ominus)$ to be large). This can be put in the form of the inequality 10. We can rewrite (10) in the form of (11) and then into the form of (12), where K is the ion pair dissociation constant for the equilibrium represented in equation 13. Known ion pair dissociation constants are in the neighborhood of 10^{-7} in acetic acid solvent.[20] Thus, an estimate of $(X^\ominus)$ in a 0.01 M solution of LiX is *ca.* 3×10^{-5} M and $(X^\ominus)/K$ is about 300. This would require k_s^{IV}/k_s^{III} to be much larger than 300. While this is unlikely, what is even less likely is to have $k_s^{IV}/k_s^{III} \gg (X^\ominus)/K$ for 3-anisyl-2-butyl but not for the 2,4-dimethoxyphenylethyl system. From what is known about the effect of structure[21] on ion pair dissociation constants, $(X^\ominus)/K$ is not expected to vary too much from system to system. Therefore, k_s^{IV}/k_s^{III} would need to change by large amounts from system to system. This amounts to a much larger effect of the $X^\ominus$ partner of the ion pair III on one system than another. This argument indicates that alternative (ii) should be rejected, leaving (i) as the explanation. Thus, IV is not formed in acetolysis of the 3-anisyl-2-butyl system. Similarly, it is not formed in acetolysis of the systems above 3-anisyl-2-butyl in Table VI.

The decision that dissociation does not compete with product-forming reaction of ion pair III for the 3-anisyl-2-butyl system has a bearing on the mechanism of the exchange reaction. The conversion of bromobenzenesulfonate to toluenesulfonate during acetolysis in the presence of toluenesulfonate ion must involve ion pairs but not dissociated carbonium ions. Formation of alkyl toluenesulfonate must involve conversion of carbonium bromobenzenesulfonate ion pair to carbonium toluenesulfonate ion pair by an exchange reaction, followed by ion pair return to covalent toluenesulfonate. This must also be the mode of formation of some of the exchange product in the case of the cholesteryl and dimethoxyphenylethyl derivatives. However, with these substances, some of the exchange involves dissociated carbonium ions.

Kinetic Appendix

Using the steady state approximation in connection with the solvolysis scheme 4, one obtains the relations 14, 15 and 16 for the steady state concentrations $(R^\oplus)$, $(R^\oplus \| X^\ominus)$ and $(R^\oplus X^\ominus)$, of the respective ionic species. The rate of formation of solvolysis product, ROS, is given by equation 17, which is converted to equation 18 by substituting for $(R^\oplus)$ its value in terms of $(R^\oplus \| X^\ominus)$ from equation 14. The rate of formation of solvolysis product may be expressed in terms of (RX) by transforming equation 18 to 19 with the aid of relations 15 and 16.

$$(R^\oplus) = \frac{k_3(R^\oplus \| X^\ominus)}{k_{-3}(X^\ominus) + k_s^{IV}} \qquad (14)$$

$$(R^\oplus \| X^\ominus) = \frac{k_2(R^\oplus X^\ominus)}{k_{-2} + k_s^{III} + k_3\left(\dfrac{k_s^{IV}}{k_{-3}(X^\ominus) + k_s^{IV}}\right)} \qquad (15)$$

$$(R^\oplus X^\ominus) = k_1(RX) \Big/ k_{-1} + k_2\left[1 - \frac{k_{-2}}{k_{-2} + k_s^{III} + k_3\left(\dfrac{k_s^{IV}}{k_{-3}(X^\ominus) + k_s^{IV}}\right)}\right] \qquad (16)$$

$$\frac{d(ROS)}{dt} = k_s^{III}\,(R^\oplus \| X^\ominus) + k_s^{IV}\,(R^\oplus) \qquad (17)$$

$$\frac{d(ROS)}{dt} = \left[k_s^{III} + k_3\frac{k_s^{IV}}{k_{-3}(X^\ominus) + k_s^{IV}}\right](R^\oplus \| X^\ominus) \qquad (18)$$

$$\frac{d(ROS)}{dt} = k_1(RX) \Big/ 1 + \frac{(k_{-1}/k_2)}{\left[k_s^{III} + k_3\dfrac{k_s^{IV}}{k_{-3}(X^\ominus) + k_s^{IV}}\right] \Big/ \left[k_{-2} + k_s^{III} + k_3\dfrac{k_s^{IV}}{k_{-3}(X^\ominus) + k_s^{IV}}\right]} \qquad (19)$$

Experimental Part

exo-Norbornyl *p*-Bromobenzenesulfonate.—This material, m.p. 55.6–56.0°, m.p. reported[12] 55.7–57.0°, 100.0 ± 0.4% pure as judged by equivalent wt. in solvolysis, was prepared as previously described.[12]

1-*p*-Anisyl-2-propyl *p*-Toluenesulfonate.—This material was the same as that employed in previous work.[13a]

DL-*threo*-3-*p*-Anisyl-2-butyl *p*-Toluenesulfonate and *p*-Bromobenzenesulfonate.—The toluenesulfonate, m.p. 49–50°, was prepared in the usual way from *dl-threo*-3-*p*-anisyl-2-butanol,[14] n^{25}D 1.5161.

Anal. Calcd. for $C_{18}H_{22}O_4S$: C, 64.65; H, 6.63. Found: C, 64.56; H, 6.59.

Similarly, the *p*-bromobenzenesulfonate, m.p. 97.5–98.5°, was prepared in 66% yield from carbinol, n^{25}D 1.5164, derived from *threo*-3-*p*-anisyl-2-butyl acid phthalate,[14] m.p. 123–124.5°.

Anal. Calcd. for $C_{17}H_{19}O_4BrS$: C, 51.13; H, 4.80. Found: C, 50.92; H, 4.70.

Cholesteryl *p*-Toluenesulfonate and *p*-Bromobenzenesulfonate.—The toluenesulfonate, m.p. 132.5–133.0°, was supplied by Kosower.[22] The *p*-bromobenzenesulfonate, m.p. 131.5–132.0°, was prepared exactly as was the *p*-toluenesulfonate.[22]

Anal. Calcd. for $C_{33}H_{49}O_3SBr$: C, 65.42; H, 8.15. Found: C, 65.64; H, 7.92.

2-(2,4-Dimethoxyphenyl)-ethyl *p*-Bromobenzenesulfonate.—The alcohol was prepared by the method of Colonge and Rochas.[23] A 113-g. quantity of aluminum chloride and 200 ml. of carbon disulfide were cooled with an ice–salt-bath, 200 ml. of 1,3-dimethoxybenzene was added, and the mixture was stirred for 2 hours. A solution of 44 g. of ethylene oxide in 200 ml. of carbon disulfide was added slowly to the reaction mixture, which was then allowed to warm to room temperature. On working up the reaction mixture in the usual way, and distillation, there was obtained a large forerun of 1,3-dimethoxybenzene and 56 g., 30%, of crude 2-(2,4-dimethoxyphenyl)-ethanol, m.p. 68–75°. Three recrystallizations of the crude *p*-bromobenzenesulfonate from this material gave a product, m.p. 71.4°, undepressed by the material prepared from alcohol derived from lithium aluminum hydride reduction of the corresponding acid.[16]

Kinetics.—Anhydrous acetic acid was prepared and acetolyses were followed as previously described[24] using brom phenol blue as indicator.

Lithium *p*-toluenesulfonate solutions were prepared by neutralization of toluenesulfonic acid solution with lithium acetate solution, acetic anhydride being employed to remove the water associated with the toluenesulfonic acid monohydrate.

Lithium *p*-bromobenzenesulfonate was prepared by hydrolysis of pure *p*-bromobenzenesulfonyl chloride with

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[20] (a) T. L. Smith and J. H. Elliott, THIS JOURNAL, **75**, 3566 (1953); (b) M. M. Jones and E. Griswold, *ibid.*, **76**, 3247 (1954).

[21] *E.g.*, (a) L. M. Tucker and C. A. Krauss, *ibid.*, **69**, 454 (1947); (b) J. B. Ramsey and E. L. Colichman, *ibid.*, **69**, 3041 (1947); (c) J. T. Dennison and J. B. Ramsey, *ibid.*, **77**, 2615 (1955).

[22] E. Kosower, Dissertation, University of California at Los Angeles, 1952.

[23] J. Colonge and P. Rochas, *Bull. soc. chim. France*, [5] **15**, 818 (1948).

[24] S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 821 (1948).

boiling water for 2 days. The aqueous solution was evaporated to dryness several times with the aid of a water-bath and an aspirator until there was obtained a negative test for chloride ion. The chloride-free acid was neutralized with lithium carbonate, and the salt was crystallized from hot ethanol-acetone as fine needles. In this solvent, the salt was more soluble at room temperature than at higher temperatures. The salt tested chloride-free and its acetic acid solution gave no test for acid or base and gave zero water titer by Karl Fischer titration.

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY]

The Influence of Polar Substituents and Polar Solvents on Radical Decomposition Reactions[1]

BY JOHN E. LEFFLER AND W. BRADFORD BOND[2]

RECEIVED JULY 25, 1955

The radical decomposition of dibenzoyl diimides and dibenzoyl peroxides is subject to polar substituent, solvent and catalytic effects resembling those observed in non-radical reactions.

Introduction

If it is assumed that the transition state and products of a radical dissociation reaction are very much like the original molecule in their charge distribution, then purely polar effects on radical dissociation rates and equilibria should be correspondingly small. Such reactions should be relatively unresponsive to substituents or at least should give a response not well correlated with that of well known heterolytic reactions. They should also be unresponsive to the polar nature of the solvent or to the addition of acidic or ionic catalysts.

If on the other hand a considerable change in charge distribution occurs during a radical decomposition reaction, then such a reaction can be expected to resemble heterolytic reactions to a considerable degree. Examples are the correlation of the rates of some undoubtedly radical dissociation reactions by means of the Hammett equation,[3] the stabilization of diradicals by acids and by Lewis acids,[4] and the well-known stability of semiquinone radicals and their nitrogen analogs in basic and acidic media, respectively.[5]

The interpretation of the rate of radical dissociation reactions is particularly difficult because of the common occurrence of radical chain transfer to the solvent. A faster decomposition in a given solvent may be the result of an acceleration of the initial decomposition or of the decomposition induced by the especially reactive radicals derived from that solvent, essentially a structural rather than a medium effect. Fast radical decompositions in polar solvents have usually been interpreted in the latter way rather than as acceleration of the initial decomposition reaction, even when no chain inhibitor is known which will reduce the rate to that in a slow solvent.

The Decomposition of Dibenzoyl Diimides

The decomposition of dibenzoyl diimide responds to polar substituents, to nucleophilic solvents and to acid catalysts and the response is, in the authors' opinion, an acceleration of the radical reaction rather than a shift to a faster heterolytic mechanism. However, it is still uncertain to what extent the nucleophilic solvents accelerate the initial radical decomposition and to what extent they merely provide better radicals for the chain decomposition. The decomposition products of the diimides are complex, numerous, and dependent on the nature of the solvent (Table I). In benzene, nitrogen is evolved and some of the products (benzoic acid and 2,5-diphenyl-1,3,4-oxadiazole) suggest the loss of an oxygen atom from dibenzoyl diimide to the benzoyl radical. Other products which may involve participation of the solvent, are benzaldehyde, biphenyl and benzoyl hydrazines. Benzoyl chloride and trichloroacetophenone are formed in carbon tetrachloride. In ethanol, ethyl benzoate and benzoic acid are formed as well as nitrogen, benzaldehyde and benzoylhydrazines.

The products and the initiation of polymerization indicate that radicals are generated in all of the solvents investigated. The kinetics are complex, a result understandable in view of the concurrent disappearance of the dibenzoyl diimide by decomposition, induced and otherwise, and by the addition of hydrogen or radicals to the azo linkage. We have not found an inhibitor capable of suppressing the complicating reactions and simplifying the kinetics. Nevertheless, the accelerating effect of electron-withdrawing substituents, of acids and of nucleophilic solvents is so large as to be unmistakable.

The solvents fall into two categories separated by orders of magnitude in the decomposition rate. The slow category includes carbon tetrachloride, benzene and benzonitrile. Benzene and benzonitrile give very much the same rate although the latter has a considerably higher dielectric constant. The fast category consists of the nucleophilic solvents such as amines and alcohols and mixtures of these with benzene, benzonitrile or carbon tetrachloride. Carbon tetrachloride–ethanol gives a very fast and autocatalytic decomposition because benzoyl chloride formed by radical attack on the carbon tetrachloride reacts with the ethanol to form hydrogen chloride, a very powerful catalyst for the decomposition. Benzene–ethanol mixtures,

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(1) This research was supported by the Office of Naval Research, United States Navy. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) This paper is based on the doctoral dissertation of W. Bradford Bond, Florida State University, 1955.

(3) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(4) J. M. Hirshon, D. M. Gardner and G. K. Fraenkel, THIS JOURNAL, **75**, 4115 (1953).

(5) L. Michaelis, *Chem. Revs.*, **16**, 243 (1935).