formation. The present results are strongly indicative that specific interactions are at least partly responsible for the deviations, but further studies of the solvent dependence of substituent effects are necessary to determine if other effects are also important. Work along those lines is continuing.

[Contribution from the Department of Chemistry, University of California, Davis, Calif.]

The Kinetics of Dissociation of the Dichlorides of Iodomethyl Sulfones

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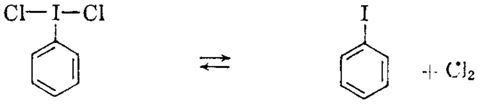
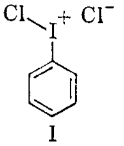
A number of iodomethyl sulfones have been prepared and converted to the corresponding iodoso chlorides ($R'SO_2CH_2ICl_2$). The rates of equilibration of these dichlorides with their components in a variety of polar solvents (acetic acid, acetonitrile and nitomethane) have been investigated by procedures used in earlier studies of iodobenzene dichloride and some of its ring substitution products. Like the iodobenzene dichlorides the iodomethyl sulfone derivatives come to equilibrium with the free iodo compounds and chlorine at easily measurable rates at room temperature, and the formation and dissociation rate constants for the two types of dichlorides are very similar. The insensitivity of these constants to changes in the nature of the organic substituent on iodine is ascribed to the high polarizability of this halogen.

Aliphatic iodides and chlorine normally form crystalline adducts[1] only at temperatures well below 0°. At higher temperatures a displacement reaction to form an alkyl chloride takes place.[2] Aromatic iodides form iodoso chlorides which can be isolated in crystalline form at room temperature. In polar organic solvents these come to equilibrium with their component iodobenzenes and chlorine (eq. 1) at easily measurable rates.[3] It has been established with reasonable certainty that the activated complexes which separate the dichlorides from their dissociation products are polarized as indicated in structure I. The positions of the three halogen atoms in these complexes have not been established unequivocally, although the proposed arrangement is favored by the authors.



(1)



I

The fact that the alkyliodoso chlorides are so unstable relative to their aryl analogs can be ascribed to the differences in susceptibilities of aliphatic and aromatic systems to attack by nucleophilic reagents. Exner[4] has discussed two alternate mechanisms (eq. 2 and eq. 3) for the decomposition of alkyliodoso chlorides to form alkyl chlorides, in which the substitution of a chlorine atom for an iodine atom on carbon occurs by processes to which he assigns, respectively, S_N2 and S_N1 character. The observation[2c,d] that reactions of this kind occur with predominant inversion is interesting in this regard, but it should not be cited as evidence that one of these reaction paths is unequivocally to be preferred to the other. It should be noted that, unlike the intermediate in eq. 3, $R\overset{+}{I}Cl\ Cl^-$ could serve adequately as a common type of intermediate in reactions leading to the formation and decomposition of aryliodoso chlorides as well as to the formation and decomposition (either to an alkyl iodide or alkyl chloride) of alkyliodoso chlorides.

$$RICl_2 \longrightarrow R\overset{+}{I}Cl\ Cl^- \longrightarrow ClR + ICl \quad (2)$$

$$RICl_2 \longrightarrow R^+ICl_2^- \longrightarrow RCl + ICl \quad (3)$$

The iodomethyl sulfones, $R'SO_2CH_2I$, constitute one class of alkyl iodides which form crystalline iodoso chlorides at room temperature.[4] Exner attributes the unusual stability of these dichlorides to one of two possible influences of the sulfonyl function. Either the $R'SO_2$– group offers sufficient steric protection[5] to the methylene carbon so that S_N2 type decomposition (eq. 2) does not occur or, because of its unfavorable inductive effect, it retards S_N1 type decomposition (eq. 3).

In the earlier investigations concerning the equilibration of aryliodoso chlorides with their components in polar media,[3] it was observed that the rate constants for dissociation of the dichlorides were relatively insensitive to the effects of ring substituents located *meta* or *para* to the reaction site. That is, the reactions to form the free iodo compounds do not appear to be markedly influenced by the organic substituents on iodine. In this connection it has seemed worthwhile to determine the effects of changes in substituents R'– on the stabilities of dichlorides of iodomethyl sulfones ($R'SO_2CH_2ICl_2$). Several new dichlorides of this type have now been prepared, and the kinetics of their equilibration reactions with the free iodo compounds and chlorine have been investigated using acetonitrile, acetic acid and nitromethane as solvents.

Experimental

The Iodomethyl Sulfones.—In general, the sulfones were prepared by the reaction of the appropriate alkane- or arenesulfinic acid sodium salts with methylene iodide. The procedures used in the preparation of iodomethyl *p*-tolyl

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[1] J. Thiele and W. Peter, *Ber.*, **38**, 2842 (1905).

[2] (a) A. Guenther, *Ann.*, **123**, 124 (1861); (b) C. Friedel, *ibid.*, **135**, 206 (1865); (c) E. J. Corey and W. J. Wechter, *J. Am. Chem. Soc.*, **76**, 6040 (1954); (d) F. M. Beringer and H. S. Schultz, *ibid.*, **77**, 5533 (1955).

[3] R. M. Keefer and L. J. Andrews, *ibid.*, **80**, 277, 5350 (1958); **81**, 5329 (1959).

[4] O. Exner, *Coll. Czechoslov. Chem. Commun.*, **24**, 3562 (1959).

[5] F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5184 (1951).

TABLE I

THE IODOMETHYL SULFONES ($R'SO_2CH_2I$)

R'–	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found	Iodine, % Calcd.	Iodine, % Found
Cyclohexyl-	90	29.17	29.10	4.55	4.51	11.13	11.26	44.05	43.64
β-Naphthyl-	139	39.77	39.43	2.73	2.80	9.65	9.57	38.21	37.84
n-Propyl-	67	19.36	19.27	3.66	3.61	12.92	12.96	51.16	50.97
2-Keto-10-camphyl-	129	37.08	37.20	4.81	4.93	9.00	9.21	35.62	36.28

sulfone and iodomethyl phenyl sulfone have been described in detail previously.[4,6]

To obtain sodium cyclohexanesulfinate a solution of cyclohexylmagnesium bromide (prepared from 0.61 mole of cyclohexyl bromide) in 400 ml. of ether was cooled to −10° and gassed with sulfur dioxide over a 25-minute period. The resultant mixture was poured onto ice and acidified with dilute sulfuric acid. The cyclohexanesulfinic acid was extracted from the aqueous solution with methylene chloride, and the extract was treated with dilute sodium hydroxide until the neutralization point was reached. The resulting aqueous phase was separated and evaporated, and the residual salt was dried at 110° for 2 hours. The 11 g. (0.064 mole) of crude sodium cyclohexanesulfinic acid (11% yield based on cyclohexyl bromide) thus obtained was refluxed and stirred with 23 g. (0.086 mole) of methylene iodide in 150 ml. of ethanol for 40 hours. The cooled reaction mixture was diluted with 100 ml. of water. The precipitate of iodomethyl cyclohexyl sulfone was recrystallized three times from aqueous ethanol; yield 5 g. (29% based on sodium cyclohexanesulfinate).

To prepare sodium 2-naphthalenesulfinate a solution of 2-naphthalenesulfonyl chloride in ethanol was refluxed with excess zinc dust for 24 hours. The unreacted zinc was filtered, and the filtrate was evaporated to dryness. The remaining zinc salt was treated with dilute sulfuric acid, and the sulfinic acid was removed from the aqueous solution by repeated extraction with methylene chloride. From this point on the procedure for recovering the sulfinic acid as its sodium salt and converting the salt to the iodomethyl sulfone was essentially the same as for the preparation of iodomethyl cyclohexyl sulfone. From 6.0 g. of sodium 2-naphthalenesulfinate 3.0 g. (36% yield) of purified (twice recrystallized from aqueous ethanol) iodomethyl β-naphthyl sulfone was obtained.

Sodium 1-propanesulfinate was prepared from *n*-propylmagnesium bromide,[7] and 38 g. of this salt was converted to iodomethyl *n*-propyl sulfone by reaction with methylene iodide by essentially the same procedure which is described above. The crude product from 38 g. of the salt was recrystallized twice from aqueous ethanol containing a trace of sodium hydrosulfite; yield of purified product 52 g. (71.5%).

Sodium 10-camphorsulfinate was prepared from *dl*-10-camphorsulfonyl chloride[8] and zinc dust by essentially the same procedure as was used in preparing sodium 2-naphthalenesulfinate except that ether was used instead of methylene chloride in extracting the sulfinic acid from its aqueous solution. From 15.0 g. of the sulfinic acid salt and excess methylene iodide 7.0 g. (31% yield) of iodomethyl 2-keto-10-camphyl sulfone, purified by three recrystallizations from aqueous ethanol, was obtained.

A sample of 2-iodoethyl *p*-tolyl sulfone was prepared from 2-hydroxyethyl *p*-tolyl sulfone[9] by a procedure described elsewhere.[10]

The properties of the sulfones which have not been prepared before are given in Table I.

Several unsuccessful attempts were made to synthesize iodomethyl *t*-butyl sulfone. Sodium 2-methylpropane-2-sulfinate was prepared from *t*-butylmagnesium chloride and sulfur dioxide by much the same procedure as was employed in making sodium cyclohexanesulfinate. After this salt was refluxed with methylene iodide in ethanol for varying lengths of time (20–50 hours), only the starting materials could be recovered. It is likely that in this case the displacement reaction to form the sulfone is subject to steric retardation to an unusual degree.

Attempts to make intermediates for the preparation of iodomethyl 10-camphyl sulfone were also unsuccessful. Camphane-10-sulfonyl chloride[11] resisted all efforts to convert it to the corresponding sulfinic acid salt by heating it with zinc dust in ethanol. Even after 24 hours of heating only the starting material could be recovered from the reaction mixture. No reaction could be induced by substitution of magnesium for zinc.

The dichlorides of the iodomethyl sulfones were prepared by gassing chloroform solutions of the iodomethyl sulfones at −10°. Precipitation of the pale yellow solids generally took place within 10 minutes. The dichlorides were filtered, washed with carbon tetrachloride and air-dried for a short period. Samples of the dichlorides were always freshly prepared immediately before use. To complete drying of the dichloride of iodomethyl phenyl sulfone, which absorbs an unusually large amount of solvent, it was found necessary to press the moist precipitate between two pieces of filter paper. The iodometric equivalent weights (Table II) of the dichlorides were determined by the procedures used in earlier work on iodobenzene dichlorides.[3]

TABLE II

PROPERTIES OF THE DICHLORIDES

$R'SO_2CH_2ICl_2$, R' =	M.p., °C.	Equiv. wt. Calcd.	Equiv. wt. Found
C_6H_5–	100–101 d.	353	361
p-$CH_3C_6H_4$–	127[a]	367	373
β-Naphthyl–	97	427	418
n-C_3H_7–	67–71 d.	319	323
Cyclohexyl–	86–87[b]	359	354

[a] In agreement with Exner,[4] who reports that the dichloride dissociates to the free iodo compound before melting occurs. [b] The melting point reported above may be characteristic of the free iodo compound (see footnote *a*), which melts at 90°.

All attempts to prepare a dichloride of 2-iodoethyl *p*-tolyl sulfone by gassing solutions of the free iodo compound in chloroform, acetic acid or carbon tetrachloride were unsuccessful. The solutions invariably became red-brown as chlorine was added. The near-ultraviolet spectrum of a freshly prepared solution of chlorine ($1.35 \times 10^{-3}M$) and the iodo compound ($1.14 \times 10^{-3}M$), which was prepared by mixing acetic acid solutions of the pure compounds, was characteristic of iodine monochloride in acetic acid. It had the typical absorption maximum[12] near 360 mμ. On the assumption that the reaction $R'SO_2CHI + Cl_2 \rightarrow R'SO_2CH_2Cl + ICl$ had occurred with quantitative conversion of the iodo sulfone to iodine monochloride, an extinction coefficient, $\epsilon_{400\ m\mu} = 112$, was calculated from the optical density of the solution at 400 mμ, after correcting for the small absorption of unreacted chlorine. For pure iodine monochloride, $\epsilon_{400\ m\mu} = 110$ in acetic acid.

The dichloride of iodomethyl 2-keto-10-camphyl sulfone could not be precipitated by gassing chloroform solutions of the free iodo compound with chlorine either at room temperature or at −20°, nor could it be separated by using acetic acid, acetonitrile or nitromethane as the solvent. In several attempted preparations the yellow reaction mixtures slowly darkened to a red-brown color. To check further on the nature of the reactions taking place, several

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(6) (a) F. C. Whitmore and F. H. Hamilton, "Organic Syntheses," Coll. Vol. I, 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 492; (b) A. Michael and G. M. Palmer, *J. Am. Chem. Soc.*, **6**, 254 (1885).

(7) P. Allen, Jr., *J. Org. Chem.*, **7**, 23 (1942).

(8) S. Smiles and T. P. Hilditch, *J. Chem. Soc.*, **91**, 519 (1907).

(9) C. C. J. Culvenor, W. Davies and N. S. Heath, *ibid.*, 278 (1949).

(10) L. Field, *J. Am. Chem. Soc.*, **78**, 96 (1956).

(11) R. B. Scott and J. B. Gayle, *J. Org. Chem.*, **21**, 391 (1956).

(12) R. E. Buckles and J. F. Mills, *J. Am. Chem. Soc.*, **75**, 552 (1953).

dilute solutions of the two reactants in acetic acid were prepared, in which the initial concentrations of the components were each in the region 5×10^{-3}–$20 \times 10^{-3} M$; the near ultraviolet and visible spectra of these solutions were investigated over an extended period of time using acetic acid as the blank. The ultraviolet absorption generally increased, as would be expected if an iodoso chloride were forming, and then eventually dropped off somewhat in intensity and a peak developed in the region of major absorption[12] (350–370 mμ) of iodine monochloride in acetic acid. When the iodo compound was initially in substantial excess of the chlorine, the absorption intensity in the near ultraviolet (370 mμ region) reached a maximum and dropped off rapidly, and as the drop took place a new visible band characteristic of iodine in acetic acid,[12] with a maximum at 478 mμ, was observed to develop. It was demonstrated by a separate spectrophotometric experiment that iodine is similarly formed when iodine monochloride reacts with iodomethyl 2-keto-10-camphyl sulfone in acetic acid. It is presumed that the iodoso chloride of this camphor derivative is unstable with respect to decomposition to form iodine monochloride and chloromethyl 2-keto-10-camphyl sulfone. Like other alkyl iodides[13] the free iodomethyl sulfone apparently can undergo a reaction of the type

$$RI + ICl \longrightarrow RCl + I_2 \qquad (4)$$

No quantitative spectrophotometric work on the reactions taking place between chlorine and the iodomethyl sulfone was conducted. Although there was some indication that an unstable dichloride was formed as an intermediate in the reaction leading to the production of iodine monochloride, this halogen and chlorine absorb strongly enough in the region of major absorption of a typical iodoso chloride so that a spectrophotometric analysis of mixtures of the three materials cannot easily be accomplished.

The Rate Measurements.—Samples of acetic acid, acetonitrile and nitromethane were purified for use as solvents in the rate work by methods to which reference is given elsewhere.[14] Eastman Organic Chemicals iodobenzene was distilled under reduced pressure and stored over mercury. Its dichloride was prepared by procedures similar to those used in the preparation of other dichlorides (see above).

The rates of equilibration of the various dichlorides with their components in the various solvents used in this investigation were established by a spectrophotometric method, a procedure which is appropriate since the dichlorides absorb in the near ultraviolet much more intensely than do chlorine and the free iodo compounds. Illustrative data are presented in Table III. The extinction coefficients reported for the dichlorides were calculated from the optical densities of freshly prepared solutions, the concentrations of which were established by iodometric analysis.

TABLE III

EXTINCTION COEFFICIENTS[a] OF THE IODO SULFONES ($R'SO_2$-CH_2I) AND THE DICHLORIDES

R'–	Solvent	λ, mμ	$\epsilon_{R'SO_2CH_2I}$	$\epsilon_{R'SO_2CH_2ICl_2}$
C_6H_5–	CH_3CN	370[b]	1.4	67.8
β-Naphthyl–	CH_3CN	390[b]	1.0	56.4
p-$CH_3C_6H_4$–	CH_3CN	390[b]	0.8	20.4
n C_3H_7–	CH_3CN	380[b]	1.6	31.7
Cyclohexyl–	CH_3CN	370[b]	0.8	66.3
C_6H_5–	CH_3COOH	370[c]	1.4	56.7
p-$CH_3C_6H_4$–	CH_3COOH	370[c]	0.8	55.4
n-C_3H_7–	CH_3COOH	370[c]	1.0	48.6
p-$CH_3C_6H_4$–	CH_3NO_2	390[d]	0.07	22.9

[a] Defined as $\epsilon = \log_{10}(I_0/I)lc$ where l is the cell path length (cm.), c is the molar concentration of the absorbing substance and $\log_{10}(I_0/I)$ is the optical density of the absorbing substance. [b] The extinction coefficients of chlorine in acetonitrile are 19.8 (370 mμ), 10.7 (380 mμ) and 7.4 (390 mμ). [c] At 370 mμ, ϵ_{Cl_2} for acetic acid is 22.0. [d] At 390 mμ, ϵ_{Cl_2} for nitromethane is 8.4.

In general, the rate samples were contained in paraffin sealed 1-cm. absorption cells which were stored in a temperature-controlled housing of a Beckman spectrophotometer during the course of the runs. Further details of the preparation of rate samples and of the methods of rate measurement for reactions in which the dichloride and also in which the iodo sulfone and chlorine were starting materials, have been discussed in previous publications.[3] In those reactions in which the dichloride was allowed to come to equilibrium with its dissociation products, the total halogen content ($[Cl_2] + [RICl_2]$) of the rate samples at equilibrium was usually determined by iodometric analysis.

In some runs in which the dichloride was used as starting material, allyl chloride or durene was included in the reaction mixture to remove chlorine as it was formed. Under the reaction conditions used the destruction of chlorine by reaction with the unsaturate or aromatic hydrocarbon was exceedingly rapid and quantitative, and the runs conducted in this fashion proceeded with complete conversion of the dichloride to the free iodo compound. Only when durene was used to remove chlorine from nitromethane solutions was this procedure unsatisfactory. The dichloride dissociation rate constants for such runs with durene increased as the reaction proceeded, although initial rates were not much affected by changes in the hydrocarbon concentrations of the media. Very likely these reactions, like the dissociation of iodobenzene dichloride, are subject to catalysis by hydrogen chloride when nitromethane is the solvent.[3]

The equilibrium constants for the dichloride equilibration process as well as the rate constants later reported for the dissociation of the dichloride both in the presence and absence of chlorine-trapping agents (durene and allyl chloride) were calculated from the spectrophotometric data by the procedures which have been used in earlier work.[3,15]

Recovery of the Iodomethyl Sulfones from Solutions of the Dichlorides.—To establish that the dissociation process was not accompanied by any major side reactions, several of the parent organic iodides were recovered from solutions of their dichlorides which had been allowed to stand for periods long enough so that equilibrium between the dichlorides and the components was established.

In a typical experiment a solution of 0.28 g. of the dichloride of iodomethyl phenyl sulfone in 10.0 ml. of acetonitrile was allowed to stand in the dark for 66 hr. The solvent and halogen were then removed from 8.0 ml. of the solution under vacuum at room temperature. A white solid residue (0.19 g.) of m.p. 58–59° and mixed m.p. with iodomethyl phenyl sulfone of 60° remained.

In a similar experiment a solution of 0.28 g. of the dichloride of iodomethyl *n*-propyl sulfone in 10 ml. of acetonitrile was allowed to stand for 2 days. After evaporation of the solvent from 8 ml. of the solution, 0.19 g. of iodomethyl *n*-propyl sulfone, m.p. 63–65°, and mixed m.p. with an authentic sample, 65–67°, was recovered.

A solution of 0.17 g. of the dichloride of iodomethyl cyclohexyl sulfone in 10 ml. of acetonitrile was allowed to stand for 48 hours after it was prepared. An 8-ml. sample was then concentrated to dryness to yield 0.12 g. of the impure sulfone, m.p. 84°. After one recrystallization from aqueous ethanol, a sample which gave a mixed m.p. of 88–89° with the pure substance was obtained.

The total halogen content of these several solutions was checked by iodometric analysis at the beginning and at the end of the standing period. In the cases of the solutions prepared from the dichlorides of iodomethyl cyclohexyl and iodomethyl phenyl sulfones the halogen analyses remained virtually unchanged during the equilibration process. In the cases of the dichlorides of iodomethyl *n*-propyl and iodomethyl *p*-tolyl sulfones the total chlorine analyses of the media dropped, respectively, to 76% and 71% of their initial values.

Results

The equilibration of the iodomethyl sulfone dichlorides with the free iodo compounds and chlorine is described by eq. 5. In Table IV the

$$R'SO_2CH_2ICl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R'SO_2CH_2I + Cl_2$$

$$K = k_1/k_2 = [R'SO_2CH_2I][Cl_2]/[R'SO_2CH_2ICl_2] \qquad (5)$$

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(13) R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **75**, 543 (1953).

(14) L. J. Andrews and R. M. Keefer, *ibid.*, **81**, 1063 (1959).

(15) R. M. Keefer and L. J. Andrews, *ibid.*, **81**, 2374 (1959).

results of the rate work on these dichlorides are summarized, and Table V presents the results of a study of the equilibration of iodobenzene dichloride with its components in acetonitrile, a solvent not previously used for this reaction.

TABLE IV

RATE AND EQUILIBRIUM CONSTANTS FOR THE DISSOCIATION OF THE IODOMETHYL SULFONE DICHLORIDES ($R'SO_2CH_2I$)

R'	Init. concn. range of dichloride, 10^3 × mole/l.	No. of runs	Temp., °C.	10^4k_1, sec.$^{-1}$	10^3K, mole/l.
			Acetonitrile solvent[a]		
p-Tolyl-	31–47	2	25.4	0.95 ± 0.02	29 ± 1
p-Tolyl-	34–51	2	45.0	6.8 ± .6	39 ± 1
Phenyl-	11–20	5	43.4	3.0 ± .8	12 ± 3
n-Propyl-	13–17	2	25.4	0.85 ± .03	12 ± 5
n-Propyl-	12–39	4	43.2	4.47 ± .14	10.4 ± 5
β-Naphthyl-	18–83	3	43.2	5.8 ± 1.0	...
Cyclohexyl-	7–21	6	43.4	3.3 ± 0.6	...
			Acetic acid solvent[b]		
p-Tolyl-	7–11	2	25.2	1.82 ± 0.05	39 ± 3
p-Tolyl-	14.9	1	45.2	12.2	98
Phenyl-	7–10	3	25.4	1.69 ± 0.10	15 ± 3
Phenyl-	7–12	2	45.0	11.4 ± .1	19 ± 2
n-Propyl-	7–27	7	25.3	2.14 ± .13	22 ± 3
n-Propyl-	13–38	5	44.8	11.2 ± .3	17 ± 8
			Nitromethane solvent[c]		
p-Tolyl-	26–40	3	45.0	3.5 ± 0.2	...
				$10^4k_1'$ sec.$^{-1}$	Init. concn. range of unsaturate, 10^3 mole/l.
			Acetonitrile solvent with allyl chloride present		
n-Propyl-	22.4	1	43.2	4.66	115
			Acetic acid solvent with durene present		
p-Tolyl-	12.1	1	25.2	2.28	87
p-Tolyl-	6.10	3	45.2	11.1 ± 1.3	60–240
Phenyl-	6.32	1	25.4	2.12	106
Phenyl-	5–8	2	45.2	14.1 ± 0.1	27–67
n-Propyl-	7.5	1	25.2	3.22	106
n-Propyl-	4–13	6	44.8	14.7 ± 2.1	60–240

[a] For iodobenzene dichloride in acetonitrile k_1 (45°) is 3.1×10^{-4} sec.$^{-1}$ (this value is calculated from average values of k_2 and K given in Table V). [b] For iodobenzene dichloride in acetic acid[3] k_1 (25°) is 1.7×10^{-4} sec.$^{-1}$ and k_1 (45°) is 14.1×10^{-4} sec.$^{-1}$. Values of K at 25° and 45° are, respectively, 1.9×10^{-3} mole/l. and 4.2×10^{-3} mole/l. [c] For iodobenzene dichloride in nitromethane k_1 (45°) is 0.71×10^{-4} sec.$^{-1}$. A value of K is not listed for *p*-tolyl iodomethyl sulfone dichloride in nitromethane, since the equilibrium reading on which the constant is based was not determined with high precision, see footnote 16.

TABLE V

RATE CONSTANTS AND EQUILIBRIUM CONSTANTS FOR THE EQUILIBRATION OF IODOBENZENE DICHLORIDE WITH ITS COMPONENTS IN ACETONITRILE[a]

$10^2[Cl_2]$, moles/l.	10^2-$[C_6H_5I]$, moles/l.	10^2-$[C_6H_5ICl_2]$, moles/l.	10^2k_2, sec.$^{-1}$ mole^{-1} l.	10^3K, moles/l.	Temp., °C.
1.34	1.63		16.5		44.7
0.613	3.26		16.1		44.7
		0.933		2.4	45.0
		1.87		2.0	45.0
		2.80		1.3	45.0

[a] In runs in which free chlorine and iodobenzene were the starting materials, their initial concentrations are given in the first two columns. The third column gives the initial reactant concentration of runs in which the dichloride was the starting material.

The constants k_1, k_2 and K reported in these tables are based in some cases on runs in which the starting materials were the free iodo compound and chlorine and in others on runs in which the dichloride itself was the initial reactant. The appropriate[3] integrated forms of the rate law

$$-d[R'SO_2CH_2ICl_2]/dt = k_1[R'SO_2CH_2ICl_2] - k_2[R'SO_2CH_2I][Cl_2] \quad (6)$$

were used in calculating the rate constants. The k_1' values reported for runs in which dissociation of the dichloride was forced to completion by conducting the reaction in the presence of reagents (durene or allyl chloride) which destroyed the liberated chlorine, are based on the rate law

$$-d[R'SO_2CH_2ICl_2]/dt = k_1'[R'SO_2CH_2ICl_2] \quad (7)$$

In both acetic acid and acetonitrile the k_1 values are remarkably insensitive to changes in the nature of substituents R' of the iodomethyl sulfone. In fact the k_1 values for reaction in acetic acid are very close to those (footnote *b*, Table IV) for the dissociation of iodobenzene dichloride in this solvent, and k_1 at 45° for iodobenzene dichloride in acetonitrile (footnote *a*, Table IV) differs from the corresponding constants for the several iodomethyl sulfones by a factor of only slightly larger than two in the most extreme case. For the reaction in nitromethane, k_1 at 45° for the dichloride of iodomethyl *p*-tolyl sulfone is about five times as large as that for iodobenzene dichloride (footnote *c*, Table IV).

The k_2 values for the iodomethyl sulfone dichlorides cannot be reported with high reliability in most cases because of uncertainties in the values of the equilibrium constants, K, which are needed for evaluation of the rate constants. These uncertainties result because very slow side reactions in which chlorine is consumed interfere with the determination of the equilibrium position for dichloride formation.[16] It can be stated qualitatively that k_2 values (k_1/K in Table IV) are somewhat more sensitive than k_1 values to changes in the structures of the dichlorides, but the variations in the dissociation rate constants of the compounds investigated do not seem to be very large. The k_2 value (45°) for the most reactive dichloride considered in this investigation (iodobenzene dichloride) is only about thirty times that for the least reactive compound (iodomethyl *p*-tolyl sulfone dichloride) when acetic acid is the solvent, and the ratios of the k_2 values (45°) for these two compounds in acetonitrile is of the order of ten. As has been noted in previous work on the iodobenzene dichlorides, the rate constants k_1 and k_2 do not change markedly when the solvent is changed from acetic acid to nitromethane, nor are they much affected when acetonitrile is substituted for either of these solvents. As is the case for the iodobenzene dichlorides, the equilibration reaction of the iodomethyl sulfone dichlorides is extremely slow in a non-polar solvent at normal temperatures. It

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(16) Since the iodomethyl sulfone dichlorides are rather highly dissociated, the accuracy of k_1 values is not much affected by the uncertainties in K. It should be noted that k_1' values for reactions in the presence of additives which destroy chlorine (durene or allyl chloride) are in good agreement with k_1 values for runs in which the additives were absent.

has been found, for example, that no spectrophotometrically detectable reaction to form a dichloride occurs in a solution of chlorine (0.06 *M*) and iodomethyl *n*-propyl sulfone (0.012 *M*) in carbon tetrachloride for a period of at least one hour after its preparation. This is sufficient time to allow for completion of the equilibration process when acetic acid is the solvent.

It is assumed, in considering the reasons for the relatively small variations in these rate constants with changes in reactant structures, that the activated complexes for the equilibration reactions of the iodomethyl sulfone dichlorides are structurally similar to those for the corresponding reactions of the iodobenzene dichlorides. That is, the activated complexes are presumed to be substantially more polar (structure I) than are the dichlorides or their components in the ground states, and this assumption is supported by the finding that the reactions are much slower in non-polar than in polar media.

The rate of a polar process in which a carbon atom is the center of reaction is generally dependent on the capacities of substituents at or near that center to support activation electronically. The sensitivity of rate to changes in substituents varies widely from reaction to reaction. However, in situations in which the activated complex is significantly more ionic in character than the reactants, changes in the inductive influences of substituents are readily apparent.[17]

The relative insensitivity of the rate constants for the equilibration reactions of the iodoso chlorides (particularly as evidenced in the values of k_1 for reaction in acetic acid) to the change in the iodine substituent from phenyl to the comparatively strongly electron-withdrawing alkyl- or aryl-sulfonyl groups[18] is, therefore, to be contrasted with the typical behavioral pattern for polar reactions involving bonds to carbon. It should be recalled again in this connection that the equilibration rates of *meta* and *para* substituted iodobenzene dichlorides also are not much affected by changes in the nature of the ring substituents. The difference in sensitivity of the reactions at carbon and iodine to substituent effects is tentatively ascribed to the differences in polarizability of these two atoms. That is, it has been concluded that an atom (*e.g.*, iodine) which is highly polarizable is not much subject to the electronic effects of nearby groups when it serves as the site of a polar reaction.

It is interesting to note that there is evidence from previous studies of the influence of solvents on reactivities,[19] that solvation of the positive end of the I–Cl dipole (the iodine) of the activated complex is an important feature of the iodobenzene dichloride equilibration reaction. On the other hand, solvation of the positive end of the activated complex is relatively unimportant in the ring chlorination of an aromatic hydrocarbon, when the conditions are such that the reaction rate is highly sensitive to electronic influences of ring substituents.[14,17] In the activated complex for this latter reaction the positive charge presumably is distributed over the entire aromatic nucleus, while in dichloride equilibration the development of positive charge on activation seems to be confined largely to a single atom in the molecule. As seems reasonable, a polar solvent must have a considerably more important role in the development of a localized than of a dispersed charge.

Thermodynamic Constants.—The energies and entropies of activation for dissociation (E_1 and $\Delta S_1^{\ddagger}$) of the compounds of formula $R'SO_2CH_2ICl_2$ are reported (Table VI) in those instances in which reasonably reliable rate constants at both 25° and 45° (Table IV) are available. In accord with the observation that k_1 values do not change much with differences in substituents (R′), the E_1 and $\Delta S_1^{\ddagger}$ values for the reactions in acetic acid are relatively independent of the structure of the dichlorides and are similar to those for iodobenzene dichloride and for several of its ring-substituted derivatives.[3] The two sets of values reported for reaction in acetonitrile are also similar to each other. No values of E_2 and $\Delta S_2^{\ddagger}$ are reported because of the relatively large errors inherent in the evaluation of k_2 for the iodomethyl sulfone dichlorides.

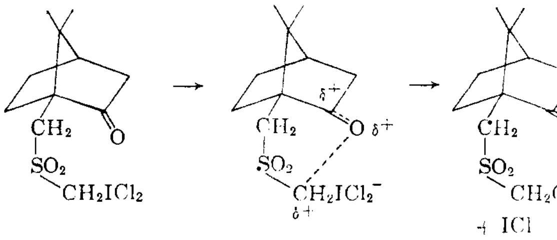
TABLE VI

ENERGIES AND ENTROPIES OF ACTIVATION FOR DISSOCIATION OF $R'SO_2CH_2ICl_2$

R′–	10^3k_1, (45°), sec.$^{-1}$	E_1,[a] kcal./mole	$\Delta S_1^{\ddagger}$,[b] e.u.
	Acetic acid solvent		
p-Tolyl–	1.22	18.0	−17.3
Phenyl–	1.14	18.4	−16.0
n-Propyl–	1.12	16.0	−23.6
[c]	1.41	19.6	−12.0
	Acetonitrile		
p-Tolyl–	0.68	19.0	−15.4
n-Propyl–	0.55	17.5	−20.5

[a] The estimated error is ± 1 to 1.5 kcal./mole. [b] The estimated error is ± 3 to 5 e.u. [c] The values reported are for iodobenzene dichloride.

The Reactions of Iodomethyl 2-Keto-10-camphyl Sulfone and 2-Iodoethyl *p*-Tolyl Sulfone with Chlorine.—As noted in the Experimental section, all attempts to prepare a dichloride of 2-iodoethyl *p*-tolyl sulfone were unsuccessful. Instead, reaction between the halogen and the iodomethyl sulfone occurred to produce iodine monochloride and presumably also the corresponding chloromethyl sulfone. That is, the stabilizing influence of a sulfonyl substituent, which prevents the breakdown of $R'SO_2CH_2ICl_2$ to iodine monochloride and other products, is exerted through one but not through two carbon atoms (as in $R'SO_2CH_2CH_2$-



(8)

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ICl_2). More surprising is the fact that a stable dichloride of iodomethyl 2-keto-10-camphyl sulfone could not be prepared. There is some spectrophotometric evidence that the dichloride has a transitory existence in solution, but it decomposes rapidly to liberate iodine monochloride and iodine. It is suggested that this dichloride may be unusually susceptible to decomposition because the carbonyl oxygen can serve (eq. 8) as a participating substituent in a process similar to that represented by eq. 3.

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Determination of Equilibrium Constants of Silver–Olefin Complexes Using Gas Chromatography

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Equilibrium constants for the formation of complexes of silver nitrate with compounds containing carbon–carbon unsaturation have been determined by a simple, rapid technique involving gas chromatography. The results indicate the strong influence of strain and steric effects on the values of these constants.

The weak interaction between silver ions and certain organic molecules containing carbon–carbon unsaturation was first quantitatively studied by Winstein and Lucas[1] in 1938. The complexes formed with these compounds and silver ion are generally quite unstable and studies on the equilibrium constants of these reactions have generally been carried out by measuring the partitioning of the olefin between an aqueous silver nitrate phase and carbon tetrachloride. This past work has been done principally by three groups: Lucas dealt chiefly with studies of aliphatic monoölefins[1,2] and some alkynes,[3] while Keefer and Andrews have been concerned with aromatic compounds,[4] and lately Traynham has investigated alicyclic olefins.[5]

This paper describes a new technique for the measurement of the equilibrium constants for the silver complex reaction that is more rapid and simpler to carry out than the older methods. This technique makes use of the relationship between the complexing equilibrium constants and retention times observed for olefins using silver nitrate–ethylene glycol gas chromatographic columns. By use of this method, new equilibrium data for the complexing reaction with silver nitrate in ethylene glycol have been obtained for a large number of aliphatic and alicyclic olefins as well as some alkynes and aromatic compounds. The equilibrium constants are found to be strongly affected by olefin structure and these variations are discussed in terms of steric, strain and electronic effects.

Development of Method

Varying retention times for different materials on a gas chromatography column are a reflection of the different partition coefficients for each material between the stationary liquid and the mobile vapor phase. The partition coefficient, H, is defined

$$H = \frac{\text{concn. of sample in liquid phase}}{\text{concn. of sample in carrier gas}}$$

This coefficient is obtained from measurable quantities by the equation[6]

$$H = \frac{3/2\left[\frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1}\right] F_c t_r}{V_L}$$

where

p_i = absolute inlet pressure
p_o = absolute outlet pressure
F_c = flow rate, corrected for temperature
V_L = volume occupied by liquid phase
t_r = time between air peak and sample peak

Evidence that this partition coefficient can be related to equilibrium processes has been given by Porter, Deal and Stross.[7] Furthermore, the obtainment of symmetrical peaks indicated that initial concentrations on the column were sufficiently low so that operation was near ideal.[7]

Next, consider what occurs when an olefin passes through a gas chromatographic column. For a column containing only a pure substrate, the following equilibrium is set up

$$(U)_V \rightleftarrows (U_L);\ K_L = (U)_L/(U)_V = H$$

where

$(U)_L$ = concn. of olefin in liquid phase
$(U)_V$ = concn. of olefin in vapor phase
K_L = equilibrium constant for pure liquid substrate

Now if the stationary liquid phase contains a solute (*i.e.*, a metal salt), two effects are possible. One is a salting-out effect due to a reduction of solubility in the liquid phase of any substance in the vapor phase. When all other factors are

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