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d-Orbital Resonance. III. Deuterium Exchange in Methyl "Onium" Salts and in Bicyclo[2.2.1]heptane-1-sulfonium Iodide¹BY W. VON E. DOERING² AND A. KENTARO HOFFMANN²

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The rates of deuterium-catalyzed deuterium exchange of tetramethylammonium (N⁺) ion, tetramethylphosphonium (P⁺) and trimethylsulfonium (S⁺) have been measured at two temperatures. From the second-order rate constants heats and entropies of activation have been calculated; N⁺: ΔH_{ex} 32.2 kcal., ΔS^\ddagger -15 cal./deg.; P⁺: 25.6 kcal., +4 cal./deg.; S⁺: 22.4 kcal., -1 cal./deg. The difference between P⁺ and N⁺ affords strong support to the hypothesis that d-orbital resonance is lowering the energy of the P⁺ transition state. Single exchanges at 62° were determined for tetramethylarsonium (As⁺) and stibonium (Sb⁺) ion and trimethylselenonium (Se⁺) and telluronium (Te⁺) ions. There is a falling off of the rate in both series which seems to be related to the increasing bond distance. The bicyclic sulfonium salt, bicyclo[2.2.1]heptane-1-sulfonium ion, exchanges deuterium showing that this molecule presents no geometrical barrier to the operation of d-orbital resonance.

The problem of determining the importance of d-orbital resonance in the organic chemistry of elements below the first row of eight essentially demands a quantitative evaluation of the interaction of the heteroelement with the organic moiety. This interaction may be observed either in stable molecules and intermediates or it may be inferred from a change in energy of transition states. There is at the present time little question that more than the complement of eight electrons normal for first row elements can be assumed by elements of the second row and below.³ But there remains considerable interest in identifying those systems in which the valence shell is expanded or, more precisely, in determining the quantitative energetic significance of expansion in particular systems.

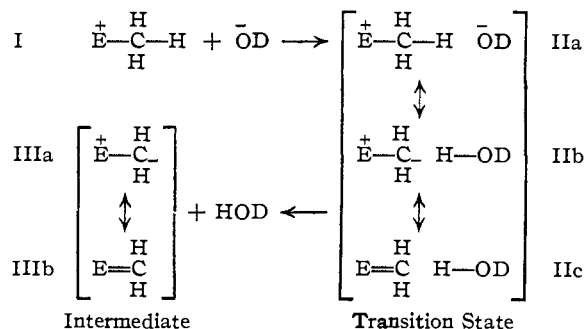
The extensive investigations in the literature designed to demonstrate the importance of d-orbital resonance in the sulfone group and in the interaction of this group with organic chemical groups such as the carbon-hydrogen bond, the carbon-carbon double bond and the carbanion have been reviewed in the two previous papers of this series.^{4,5} These investigations have suffered from the lack of a completely acceptable non-resonating standard with which the sulfone group may be compared. Consequently reasonably precise experimental estimations of the quantitative effect of d-orbital resonance in the organic chemistry of the sulfone group are lacking, although much evidence points to the importance of d-orbital resonance in the sulfone group itself.

The synthesis of the bicyclic trisulfone by Doering and Levy⁴ had been designed to provide a non-resonating standard by creating a geometrically special situation which might restrict the operation of d-orbital resonance provided, of course, this resonance had a violable geometrical requirement. The results of this investigation, although indicative, were inconclusive.

Searching for a system where an acceptable non-resonating standard would be available, Doering

and Schreiber⁵ examined the vinylsulfonium and vinylammonium ions and discovered that the vinylsulfonium ion adds bases readily in a new reaction, whereas the vinylammonium ion does not. This striking difference in behavior of the vinylammonium and vinylsulfonium ion (the latter adding bases at least 10⁵ times faster than the former) was interpreted as strong indication of the importance of d-orbital resonance in the stabilization of an α -carbanion by adjacent sulfonium. From a theoretical point of view this work suffered from two weaknesses. First the positively charged nitrogen atom, being in group V of the periodic table, was not the best model for comparison with a positively charged sulfur atom (group VI). Second, no quantitative expression of the difference between the stabilizing effect of the two positively charged atoms was determined, only a lower limit being obtained. Part of the subject of the present paper is the removal of these two theoretical deficiencies.

Measurements of the kinetics of the deuterium-catalyzed exchange of deuterium in deuterium oxide solutions of methyl "onium" salts I was the reaction chosen for further study. Although no reaction of this exchange type had been reported in the literature, the existence of the reaction seemed almost a necessary corollary to the reaction of vinylsulfonium ions with bases. The exchange would be a simple, uncomplicated reaction, the rate of which would be determined by the difference in free energy between the starting product in deuterium oxide solution and the transition state for the exchange reaction. It was assumed that the transition state II would be the one involved in the production of an intermediate "ylid" III and that differences in heats of activation would be a reflection of the varying abilities of different E⁺ groups



(1) From a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty Pure Science of Columbia University.

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(3) See D. F. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332 (1954), and references cited therein.

(4) W. v. E. Doering and L. K. Levy, *THIS JOURNAL*, **77**, 509 (1955).

(5) W. v. E. Doering and K. C. Schreiber, *ibid.*, **77**, 514 (1955).

TABLE I
 DEUTEROXIDE-CATALYZED DEUTERIUM EXCHANGE OF METHYL "ONIUM" SALTS

Substance	Wt., g.	Vol., cc.	Salt, <i>M</i>	Deuterioxide, <i>N</i>	Time, hr.	Temp., °C.	Deuterium, atom %
(CH ₃) ₄ NI (N ⁺)	0.603	10.0	0.30	0.2920	358	100	1.13
(CH ₃) ₄ PI (P ⁺)	.197	3.0	.30	.2962	3	62	73.9
(CH ₃) ₄ AsI (As ⁺)	.236	3.0	.30	.2947	3	62	7.44
(CH ₃) ₄ SbI (Sb ⁺)	.278	3.0	.30	.2881	3	62	0.78
(CH ₃) ₃ SI (S ⁺)	.306	5.0	.30	.3076	3	62	98.0
(CH ₃) ₃ SeI (Se ⁺)	.226	3.0	.30	.2941	3	62	13.2
(CH ₃) ₃ TeI (Te ⁺)	.090	2.0	.15	.2930	3	62	3.99
<i>n</i> -Butyl sulfoxide	1.000	5.0	(1.24) ^a	2.22	120	56.4	0.45
Bicyclo[2.2.1]heptane-1-sulfonium iodide	1.220	5.0	1.00	0.3124 ^b	288	56.4	20.1

^a Only partially soluble. ^b The normality decreased to 0.2078 at the end of the reaction at which time insoluble oil was also present.

to stabilize the adjacent partial negative charge. Although this mechanism would lead to exchange, so would a concerted mechanism of the type ruled out so conclusively for the formation of carbanions from ketones by Hsü, Ingold and Wilson.⁶ Should this latter type of mechanism operate, the carbon atom in the transition state would still possess a partial negative charge, differences in the attenuation of which would likewise be discernible through kinetic investigation.

There are indications in the literature suggesting that α -protons can be removed more readily from phosphonium and sulfonium ions than from ammonium ions. Thus 9-fluorenyltrimethylphosphonium⁷ and 9-fluorenyldimethylsulfonium⁸ ion react with alkali to give the isolable, corresponding fluorenylidide whereas 9-fluorenyltrimethylammonium⁹ gives no isolable fluorenylidide but a colored solution. Wittig and Felletschin¹⁰ were, however, able to isolate the very unstable 9-trimethylammonium fluorenylidide using phenyllithium as the base. Biilmann, *et al.*, have found that ethyl α -trimethylphosphonium propionate racemizes without a catalyst¹¹ whereas the ethyl α -trimethylammonium propionate is optically stable for months¹² although it racemizes in the presence of a basic catalyst.^{12,13} Finally Wittig and Wetterling¹⁴ have succeeded in converting tetramethylammonium chloride with phenyllithium into trimethylammonium methylide whereas Schlenk and Holtz¹⁵ found that benzylsodium would not effect this reaction. One is inclined to place the acidity of N⁺ between that of benzene and toluene but neither in this example nor in the first example⁷⁻¹⁰ is it clear whether kinetic or thermodynamic control is operative. The second example¹¹⁻¹³ seems clearly to involve kinetic control.

To remove the first theoretical objection to the work of Doering and Schreiber,⁵ the extent of deuterium exchange in tetramethylphosphonium (P⁺)

ion was compared with that in tetramethylammonium (N⁺) ion. Trimethylsulfonium (S⁺) ion was included to relate deuterium exchange with the results of Doering and Schreiber. In these and the other experiments reported here the starting materials were carefully purified, a precaution that was found to be particularly necessary with P⁺, which consumed alkali on potentiometric titration unless it was purified previously by treatment with silver oxide. The exchanges were run in 99.8% deuterium oxide containing known concentrations of deuterioxide ion. The salts were recovered as the iodides, purified by crystallization, dried thoroughly and combusted to water. The deuterium content of the water was determined by the falling drop method as outlined in the Experimental section. The results of the exchange experiments on N⁺, P⁺ and S⁺ are shown in Table I. An experiment with N⁺ at 62° for 504 hr. in which there was no observable deuterium exchange is omitted as is an experiment with P⁺ in the absence of deuterioxide ion in which no deuterium was exchanged. It is clear that both tetramethylphosphonium (P⁺) and trimethylsulfonium (S⁺) undergo very much more rapid, base-catalyzed exchange than does tetramethylammonium (N⁺).

Here then is a large difference between the effect of a first and second row element on the activation of a carbon-hydrogen bond to removal by base where both heteroelements are in the same group of the periodic table. As in the comparison between vinylsulfonium and vinylammonium ions,⁵ one notes that the normal carbon-nitrogen bond distance (1.47 Å.) is considerably smaller than the normal carbon-phosphorus bond distance (1.87 Å.)¹⁶ so that purely coulombic interaction of the positive charge on the heteroelement with the partial negative charge on carbon should lead to the prediction of more rapid exchange in the tetramethylammonium ion than in the tetramethylphosphonium. From the fact that P⁺ exchanges several orders of magnitude faster than N⁺ one concludes in general terms that a factor is operating in P⁺ to a much greater extent than in N⁺ and specifically that d-orbital resonance, absent in N⁺, is the important factor in the phosphonium salt.

It is noteworthy that the use of a nitrogen analog as the non-resonating standard for comparison with the vinylsulfonium ion⁵ led, if one can extrapolate from the deuterium exchange results, to a greater

(6) S. K. Hsü, C. K. Ingold and C. L. Wilson, *J. Chem. Soc.*, 78 (1938).

(7) L. A. Pinck and G. E. Hilbert, *THIS JOURNAL*, 69, 723 (1943).

(8) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 713 (1930).

(9) C. K. Ingold and J. A. Jessop, *ibid.*, 2357 (1929).

(10) G. Wittig and G. Felletschin, *Ann.*, 555, 133 (1944).

(11) E. Biilmann and K. A. Jensen, *Bull. soc. chim. France*, [5] 3, 2306 (1936).

(12) E. Biilmann and N. Berg, *ibid.*, [5] 1, 1645, 1653 (1934).

(13) E. Biilmann, K. A. Jensen and H. B. Jensen, *ibid.*, [5] 3, 2295 (1936).

(14) G. Wittig and M.-H. Wetterling, *Ann.*, 557, 193 (1947).

(15) W. Schlenk and J. Holtz, *Ber.*, 50, 274 (1917).

(16) M. L. Huggins, *THIS JOURNAL*, 75, 4126 (1953).

TABLE II
 SECOND-ORDER RATE CONSTANTS FOR DEUTERIUM EXCHANGE

Salt	Temp., °C.	k' in sec. ⁻¹	Deuterioxide, M	k in l. mole ⁻¹ sec. ⁻¹
N ⁺	83.6 ± 0.2	9.43 ± 0.08 ^a × 10 ⁻¹⁰	0.3112	3.11 ± 0.03 × 10 ⁻⁹
N ⁺	100.0 ± .1	6.94 ± .07 × 10 ⁻⁹	.3112	2.29 ± .02 × 10 ⁻⁸
P ⁺	26.800 ± .002	2.56 ± .04 × 10 ⁻⁶	.2605	9.85 ± .20 × 10 ⁻⁶
P ⁺	56.4 ± .1	1.84 ± .04 × 10 ⁻⁴	.3868	4.82 ± .10 × 10 ⁻⁴
P ⁺	56.4 ± .1	1.21 ± .02 × 10 ⁻⁴	.2612	4.63 ± .08 × 10 ⁻⁴
S ⁺	0.0 ± .1	7.50 ± .14 × 10 ⁻⁷	.2615	2.87 ± .05 × 10 ⁻⁶
S ⁺	26.800 ± .002	3.00 ± .3 × 10 ⁻⁵	.2615	1.15 ± .11 × 10 ⁻⁴
S ⁺	26.800 ± .002	3.06 ± .05 × 10 ⁻⁵	.2615	1.17 ± .02 × 10 ⁻⁴

^a These are probable errors computed from the deviations of the points from the least squares line.

difference than would have been encountered had the vinylphosphonium ion been compared. Although one would expect this latter ion to add bases more slowly than the vinylsulfonium, it should still react much more rapidly than the vinylammonium ion.

A careful kinetic study of the deuterium exchange of N⁺, P⁺ and S⁺ was undertaken to establish quantitatively the difference between the activating effect of ammonium and phosphonium and to determine how this difference is distributed between heat and entropy of activation. Ideally a comparison involving thermodynamic control in which a free energy difference between, for example, a nitrogen and a phosphorus containing molecule could be broken down to a heat term and an entropy term would be more informative from a theoretical point of view. Lacking this a kinetically controlled reaction must serve even though the obvious disadvantage of structural effects in transition states is involved. The lack of such examples in the literature provides further impetus for the present study.

The technique for measuring the rate of deuterium exchange is described in the experimental section. A sample of the data for two duplicate runs on S⁺ is given in Table V. The reaction is demonstrated to be second order by the runs with P⁺ at two different deuterioxide ion concentrations, shown along with the other rate constants in Table II. No correction is made for the dilution of deuterium which occurs during the exchange since only very small amounts of protium are released in comparison to the total volume of deuterium oxide used. No correction for the fact that the exchange ultimately reaches equilibrium was made because no run was carried far enough to observe a downward curving deviation from the linear first-order plot. From the second-order rate constants the heat and entropies of activation were calculated in the usual way with the results being given in Table III.

 TABLE III
 HEAT AND ENTROPY OF ACTIVATION OF DEUTERIUM EXCHANGE

Salt	ΔH_{exp} , kcal.	ΔS^\ddagger , cal./°C. ^a
N ⁺	32.2 ± 0.6	-15 ± 2
P ⁺	25.6 ± .2	+4 ± 1
S ⁺	22.4 ± .5	-1 ± 2

^a Heats of activation were calculated from $\Delta H_{\text{exp}} = 2.303RT_1T_2\Delta(\log k)/(T_2 - T_1)$ and entropy of activation from $k = (KTe/h)e^{\Delta S^\ddagger/R}e^{-\Delta H_{\text{exp}}/RT}$.

The difference of 6.6 kcal. in the heat of activa-

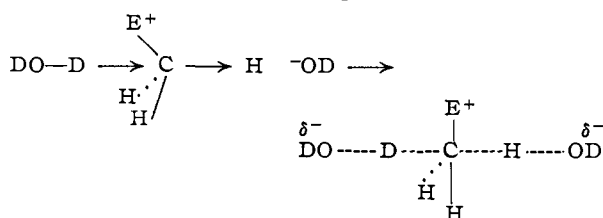
tion between N⁺ and P⁺ gives quantitative confirmation to the hypothesis expressed above that an energy factor is operating in the more rapid exchange of the second row elements. This is a minimal difference if one accepts the hypothesis that the greater activating effect in N⁺ as compared to neopentane, for example, is due solely to coulombic interaction uncomplicated by resonance. The approximate hypothesis that the coulombic interaction would be less in P⁺ by the ratio of the bond distances can be expressed in the following way. If the heat of activation in the exchange of P⁺ were due to coulombic interaction alone, it would be equal to the observed heat of activation of N⁺ multiplied by the ratio of the C-P:C-N bond distances

$$\Delta H_{\text{Cp}^+} = (\Delta H_{\text{expN}^+})r_{\text{P}^+}/r_{\text{N}^+}$$

There are many obvious, serious simplifications in this equation. However, taking C-N = 1.47 and C-P = 1.87,¹⁶ the expected heat of activation of P⁺ would be 41.0 kcal. Crude though this approximation be, it points out that the observed difference (6.6 kcal.) is much smaller than it would have been on a model in which d-orbital resonance had been inoperative. Defined in this particular way, it allows one to conclude that the contribution to the lowered heat of activation in P⁺ due to resonance is 15.4 kcal. Similarly the heat of activation of deuterium exchange due to coulombic interaction alone in S⁺ would have been 39.6 whence the actual lowering, ascribed to d-orbital resonance, is 17.2 kcal.

The large difference in rate of exchange of N⁺ and P⁺ is due in about equal measure to the differences in heat of activation and entropy of activation. In terms of an "ylid" as the intermediate the transition state will partake of the structure of the ultimate "ylid." One of the corollaries of invoking d-orbital resonance to accommodate a lowered heat of activation will be a lowered dipole moment in the "ylid" and transition state preceding it. It follows that solvent, strongly bound and well oriented in the starting state, will be more completely released in the transition state of the less dipolar phosphorus case than in that of the more strongly dipolar nitrogen. This appears clearly in the diagram above: resonance forms IIc and IIIb in the transition state and intermediate, respectively, do not participate in N⁺ and therefore leave these states with a higher dipole moment and stronger interaction with solvent than is true in the case of P⁺ or S⁺ where IIc and IIIb contribute to make the states considerably less dipolar.

It is possible that the mechanism and therefore the transition state is not as assumed above but involves a concerted one-step mechanism in which



no free "ylid" is formed. Such a difference would affect in the main only the size of the partial negative charge on carbon in the transition state. The arguments about the differences in heat and entropy of activation would remain unchanged.

It is possible, however, that the difference in heat and entropy of activation between N^+ and P^+ (and S^+) is due to the operation of different mechanisms. In that event one could conclude that the different mechanism by which N^+ reacted represented a path of lower free energy of activation than the path involving the P^+ mechanism. Specifically, if one grant that P^+ reacts by the two-step "ylid" process, then reaction of N^+ by a different mechanism, for example, the one-step mechanism, would predict an even greater difference in rates had N^+ reacted by the same mechanism as P^+ .

The effect of passing further down the periodic table being of interest, deuterium exchange was extended to include tetramethylarsonium (As^+) and tetramethylstibonium (Sb^+) in group V and trimethylselenonium (Se^+) and trimethyltelluronium (Te^+) in group VI. Although it would have been very much more significant to determine the complete kinetic behavior of these salts, due to physical limitations only single point runs were made. These results are shown in Table I. In both groups the rates decrease down the periodic table. The facility of these exchanges is not only of interest in itself but should be useful in permitting one to predict new base-catalyzed reactions of "onium" salts. These reactions should be comparable to the reactions in which carbanions partake.

On the thought that this decrease may be related to the increasing bond distance, rate constants, obviously very rough, were calculated for all salts at 62° and these were treated by an equation similar to that used above

$$\log k_{\text{E}^+} = (\log k_{\text{N}^+})r_{\text{E}^+}/r_{\text{N}^+} - R_d$$

Although it would have been far preferable to have the heats of activation, in their absence one can proceed on the assumption that the entropies of activation of the salts other than N^+ are essentially constant. The results, shown in Table IV, are in remarkably good agreement with the hypotheses expressed in the equation above; that the falling off in rate is due to the effect of increasing bond length in decreasing the coulombic lowering of the activation energy; and that the contribution of d-orbital resonance (R_d) remains roughly constant throughout. This latter hypothesis does not seem unreasonable in the light of the rather small decrease in strength shown by sigma bonds with increasing length. As an example, the energies of

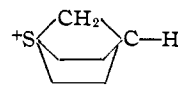
the bonds between carbon and the group V elements would be most appropriate but these are not known beyond the C-N bond. The energies of the group V halides, taken from the compilation of Huggins,¹⁷ are illustrative; P-, As- and Sb-Cl: 78.5, 73.1, 74.3, respectively; P-, As- and Sb-Br: 63.7, 58, 62; and P-, As- and Sb-I: 49, 42, 44.

TABLE IV

Salt	$\log k_{\text{E}^+}^a$	$(\log k_{\text{N}^+})r_{\text{E}^+}/r_{\text{N}^+}$	$r_{\text{E}^+}, \text{\AA}^b$	$R_d, \text{kcal.}^d$
N^+	-9.75	(-9.75)	1.47	0.0
P^+	-3.37	-12.39	1.87	13.8
As^+	-4.61	-13.12	1.98	13.1
Sb^+	-5.62	-14.46	2.18 ^c	13.6
S^+	-2.44	-12.00	1.81	14.7
Se^+	-4.09	-12.87	1.94 ^c	13.5
Te^+	-4.63	-14.26	2.15 ^c	14.8

^a Calculated from known rates and heat of activation (N^+ , P^+ , S^+) and in the remaining cases from the single point in Table I. ^b Taken from Huggins.¹⁶ ^c Calculated on the basis of Huggins' figures¹⁶ and the equation $r_{\text{AB}} = r_{\text{AP},\text{A}} + r_{\text{BP},\text{B}}^{-0.09} |X_{\text{A}} - X_{\text{B}}|$. ^d Calculated from the equation, $[\log k_{\text{E}^+} - \log k_{\text{N}^+} (r_{\text{E}^+}/r_{\text{N}^+})] (2.303RT/1000)$.

The theoretical work of Kimball¹⁸ and Koch and Moffitt¹⁹ indicates that there is little if any angular requirement for d-p overlap. Continuing the experimental investigation of this matter begun by Doering and Levy,⁴ we have examined deuterium exchange in bicyclo[2.2.1]heptane-1-sulfonium ion. The molecule was not completely stable in alkali so



that deuterium-catalyzed exchange could be carried out for a limited time only and the result, given in Table I, is of value only in showing that exchange does occur. Although there is no indication that all six exchangeable hydrogen atoms exchange at the same rate, it is clear that the special geometrical constraint of the bicyclic sulfonium salt has not drastically inhibited d-orbital resonance. This outcome is in accord with theoretical prediction.^{18,19}

Finally butyl sulfoxide was found to exchange quite slowly. This result indicates that there is some activation by sulfoxide in contrast to the impression based on the finding of Shriner, Struck and Jorison²⁰ that two sulfoxide groups failed to confer measurable acidity on an adjacent methylene group. By way of comparison dimethylsulfone seems to exchange much more rapidly.²¹

Experimental²²

Tetramethylammonium Iodide (N^+).—Prepared from trimethylamine and methyl iodide, N^+ was crystallized from water until analytically pure.

Anal. Calcd. for $\text{C}_4\text{H}_{12}\text{IN}$: C, 23.9; H, 6.0; I, 63.1; N, 7.0. Found: C, 23.9; H, 5.8; I, 62.9; N, 6.9.

(17) M. L. Huggins, *THIS JOURNAL*, **75**, 4123 (1953).

(18) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

(19) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

(20) R. L. Shriner, H. C. Struck and W. J. Jorison, *THIS JOURNAL*, **52**, 2080 (1930).

(21) J. Hochberg and K. F. Bonhoeffer, *Z. physik. Chem.*, **A184**, 419 (1939).

(22) M.p.'s are corrected. Microanalyses are by the Schwarzkopf Microanalytical Laboratory, 56-19 37th Avenue, Woodside 77, New York.

Tetramethylphosphonium Iodide (P⁺).—An ethereal solution of trimethylphosphine was prepared from 1.5 moles of methylmagnesium iodide (from 36 g. of magnesium and 213 g. of methyl iodide) and 45 g. of phosphorus trichloride according to Mann and Wells.²³ This solution was treated with 47 g. of methyl iodide for 48 hr. The crude P⁺, 30.0 g., m.p. 312–322° with dec. in a sealed capillary, smelled of trimethylphosphine, gave a colorless precipitate on treating with aqueous sodium hydroxide and on potentiometric titration consumed appreciable quantities of alkali. It was purified by dissolving 10 g. in 250 cc. of water, boiling in a stream of nitrogen passing through (8 hr.) until the effluent vapor no longer smelled of any phosphine or gave a red color with carbon disulfide, adding 2.5 g. of silver oxide and boiling again in a stream of nitrogen for 6 hr. During this time water was added as needed. The solution was neutralized with hydriodic acid and evaporated to dryness *in vacuo*. The residue was recrystallized from 1:1 ethanol-acetonitrile to give 8.0 g. (33% based on phosphorus trichloride) of pure P⁺, m.p. over 360° in a sealed capillary. The potentiometric titration curve of this material with alkali was indistinguishable from that of potassium chloride.

Anal. Calcd. for C₄H₁₂IP: C, 22.0; H, 5.6; I, 58.2; P, 14.2. Found: C, 22.1; H, 5.5; I, 58.2; P, 13.8.

Tetramethylarsonium Iodide (As⁺).—To a solution of 70 g. of dimethylcadmium²⁴ in 100 cc. of anhydrous ether in a three-necked, ice-cooled flask fitted with a downward condenser, 59 g. of arsenic trichloride in 100 cc. of ether was added dropwise with stirring over 4 hr. After 2 more hours of stirring, the reaction mixture, containing a white precipitate, was treated with 200 cc. of concentrated ammonia and heated gently in a bath to 65° until distillation ceased. The distillate, warmed to room temperature to remove ammonia, was treated with 50 g. of methyl iodide in 100 cc. of ether for 12 hr. Four recrystallizations of the precipitate from absolute ethanol afforded 50 g. (55%) of As⁺; m.p. 333–336° in a sealed capillary placed in a m.p. block at 250° and heated at 1° per min.; reported²⁶ m.p. 328° with dec.

Anal. Calcd. for C₄H₁₂AsI: C, 18.4; H, 4.6; As, 28.6; I, 48.5. Found: C, 18.8; H, 4.8; As, 28.7; I, 48.3.

Tetramethylstibonium Iodide (Sb⁺).—The addition of 60 g. of antimony trichloride in 100 cc. of ether to methylmagnesium iodide (1.0 mole) cooled in ice was effected by a modified procedure of Hibbert.²⁵ The reaction mixture was then treated with 100 cc. of 5 N potassium hydroxide and distilled until water began to condense. The distillate was treated with 20 g. of methyl iodide for 7 days. The crude Sb⁺ (20 g.) consumed alkali on titration and was purified in the same way as was P⁺ above. Recrystallization from ethanol of the salt recovered from the silver oxide treatment removed insoluble material and afforded long needles of pure Sb⁺, 17.5 g. (20%), decomposing between 288 and 302° in a sealed capillary. The potentiometric titration curve of the salt with alkali was indistinguishable from that of potassium chloride of equal normality.

Anal. Calcd. for C₄H₁₂ISb: C, 15.6; H, 3.9; I, 41.1. Found: C, 15.9; H, 4.0; I, 41.2.

Trimethylsulfonium Iodide (S⁺).—Methyl mercaptan was passed into a solution made from 10 g. of sodium and 500 cc. of methanol until saturated. To the ice-cooled solution 35 g. of dimethyl sulfate was added slowly. After 3 standing hours, dimethyl sulfide was distilled and treated directly with 45 g. of methyl iodide in 100 cc. of ether. After 16 hr., the sulfonium salt was filtered and recrystallized from ethanol; 45.0 g. (80%), m.p. 193–194° with dec. in a sealed capillary.

Anal. Calcd. for C₃H₉IS: C, 17.7; H, 4.4; I, 62.2; S, 15.7. Found: C, 17.9; H, 4.5; I, 62.0; S, 15.4.

Trimethylselenonium Iodide (Se⁺).—Following the procedure of Emelús and Heal,²⁷ 20.0 g. of selenium and 106 g. of methyl iodide were heated for 8 hr. at 220° in a sealed tube to give a viscous oil which was dissolved in a mixture of 200 cc. of ethyl acetate and 200 cc. of water. The solution was treated with hydrogen sulfide until colorless, filtered and poured into 4 l. of acetone to precipitate the

crude salt (50 g.). After recrystallization from ethanol, the salt (22 g.) melted at 150–151° in a sealed capillary introduced in the m.p. block at 130° and heated at 0.5° per min. The salt is quite volatile and is best purified by dissolving in ethanol and reprecipitating with ether or dioxane.

Anal. Calcd. for C₃H₉ISe: C, 14.4; H, 3.6; I, 50.6; Se, 31.5. Found: C, 14.4; H, 3.7; I, 50.5; Se, 31.7.

When 1.50 g. (0.006 mole) of this salt in 10.00 cc. of 0.6034 N sodium hydroxide (0.006034 mole) was maintained at 62° for 12 hr., 0.00223 mole of alkali was consumed.

Trimethyltelluronium Iodide (Te⁺).—Prepared according to Vernon,²⁸ dimethyltelluride (from 100 g. of dimethyltelluronium diiodide) was distilled directly into a cooled flask containing 40 g. of methyl iodide to give 60 g. of crude, yellow Te⁺ which became colorless after five recrystallizations from water; 40 g. (55% yield), m.p. 240–241° with dec. in a sealed capillary.

Anal. Calcd. for C₃H₉ITe: C, 12.0; H, 3.0; I, 42.4. Found: C, 12.3; H, 3.3; I, 42.2.

A solution of 0.006 mole of this salt in 10 cc. of 0.6034 N sodium hydroxide consumed 0.00079 mole of alkali on standing at 62° for 12 hr.

Butyl Sulfoxide.—Prepared according to Saytzeff and Grabowsky,²⁹ the sulfoxide melted 33.8–35.0° (reported²⁹ m.p. 32°).

Bicyclo[2.2.1]heptane-1-sulfonium Iodide.—4-Carboethoxytetrahydrothiapyran was prepared according to the procedure of Hanousek and Prelog³⁰ and Prelog and Cerkovnikov³¹ and was reduced by adding dropwise a solution of 10.0 g. of the ester in 100 cc. of ether to 6.0 g. of lithium aluminum hydride in 400 cc. of ether. Hydrolysis of the reaction mixture with 50% aqueous sulfuric acid gave a granular precipitate the ether-washings of which were united with the original ether phase, washed with aqueous potassium carbonate and dried over anhydrous potassium carbonate. Distillation afforded 6.5 g. (85% of 4-hydroxymethyltetrahydrothiapyran; b.p. 135° at 17 mm., reported³¹ b.p. 138° at 18 mm., *n*_D²⁰ 1.5213, *d*₄²⁰ 1.0884, *M*_R calcd. 37.3 (found 36.9).

Converted according to Prelog and Cerkovnikov,³¹ 1.0 g. of this material yielded 0.98 g. (85%) of bicyclo[2.2.1]heptane-1-sulfonium chloride much too hygroscopic for convenience. An aqueous solution of this salt (0.90 g.) was converted to the hydroxide, with silver oxide, filtered from the silver salts, neutralized with hydrogen iodide and evaporated to dryness. The residue was recrystallized from absolute ethanol to give 1.4 g. (96%) of bicyclo[2.2.1]heptane-1-sulfonium iodide; m.p. 243.5–244.5°.

Anal. Calcd. for C₇H₁₁IS: C, 29.7; H, 4.5; I, 52.4; S, 13.2. Found: C, 30.0; H, 4.7; I, 52.2; S, 13.0.

In contrast to trimethylsulfonium iodide, the bicyclic sulfonium salt decomposes partially on heating at 56° for 288 hr. with 0.31 N alkali.

Deuterium Analyses.—The method of the falling drop³² was used for deuterium analysis, with slight changes in combustion tube packing. Combustion tubes were packed with 7 to 8" of 0.001" platinum wool and about 3 in. of fine electrodeposited silver crystals. Experiments with standards showed these trains to have no "memory." Following each combustion, the trains were reconditioned and allowed to flush overnight with oxygen prior to introducing the next sample. After continued use, the platinum lost activity and could be regenerated by boiling in concentrated nitric acid.

Water obtained from combustion was purified by refluxing over chromic oxide followed by distillation from barium carbonate. All distillations were effected *in vacuo* in traps which had been washed with acid, rinsed with ammonia, steamed, dried and flamed *in vacuo* before use.

In those cases where deuterium oxide content exceeded 5% by weight, purified sample water was diluted with pure water by weight.

The pipet used for sample analyses was made of Pyrex capillary tubing; 27 cm. long; o.d. 5 mm.; i.d. less than

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(25) W. Steinkopf and G. Schwen, *ibid.*, **54**, 1437 (1921).

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(29) A. Saytzeff and N. Grabowsky, *Ann.*, **175**, 348 (1875).

(30) V. Hanousek and V. Prelog, *Collection Czechoslov. Chem. Commun.*, **4**, 259 (1932).

(31) V. Prelog and E. Cerkovnikov, *Ann.*, **537**, 214 (1939).

(32) A. S. Keston, D. Rittenberg and R. Schonheimer, *J. Biol. Chem.*, **122**, 227 (1937).

0.5 mm. The tip, drawn to an o.d. of 2 mm. was ground to an angle of 60° from horizontal. The ground section was 1-2 mm. long and flat at the bottom. The upper end of the tube was fluted to accept the joint of a 1-ml. syringe which was attached with Kroinig cement. The tube was mounted in a microscope stand for easy raising and lowering. The tube was filled with mercury and the syringe plunger, lubricated with Celvacene Heavy grease, was forced into the barrel about half way. Graduations on the tube provided a means of expressing a constant sample volume, the drop size being 4.2 cmm.

A center-cut of fractionally distilled Eastman "White Label" *o*-fluorotoluene equilibrated with water at 26.8° was used as the dropping medium in a bath at 26.800 ± 0.002°. The analyses of the single points reported in Table I are from a calibration curve based on the dropping times of 0.00, 1.03, 3.07 and 7.11% by weight deuterium oxide, while the analyses of the kinetic points are from a curve based on 0.000, 0.100, 0.302, 0.509, 0.802, 1.08, 1.82, 3.22, 4.01 and 5.18% by weight deuterium oxide.

Throughout the course of analyses reference was made to the dropping rates of standard samples. A microbalance was used for the dilution of the samples in the kinetic runs, but not for the single point exchanges. On the basis of duplicate analyses, it is estimated that the error in single point exchanges is about 5%. This method agreed well (within 3%) with a mass spectroscopic analysis of a standard sample of lauric acid-*d*.³⁴

Combustion of undeuterated samples of each salt ensured that the water purification procedure was operative; in each case pure water was isolated.

A blank exchange run was carried out on a 0.3 *M* deuterium oxide solution of tetramethylphosphonium iodide containing no deuterium ion for 3 hr. at 62°; completely undeuterated starting material was recovered.

Single Point Deuterium Exchanges.—Sodium deuterioxide solutions were prepared by dissolving clean sodium in 99.8% deuterium oxide (Stuart Oxygen Co., San Francisco). The sodium, weighed in nitrogen-filled weighing flasks, was added to the deuterium oxide in a flask protected by a condenser and Ascarite tube and frozen in a Dry Ice-bath. The deuterium oxide was allowed to warm slowly whereupon the reaction began and the flask was immediately reimmersed in Dry Ice. In the amounts shown in Table I the salts were dissolved in the specified volumes of sodium deuterioxide solution with the exception of the tetramethylammonium salt. This solution was prepared by stirring the iodide in 5 cc. of deuterium oxide with 0.78 g. of powdered silver oxide, stirring with an additional 5 cc. of deuterium oxide, centrifuging and decanting. The temperature, time of heating and normality of deuterioxide are given in Table I. The amount of exchange is reported as atom per cent. deuterium which is equal to the per cent. deuterium in the water of combustion. All the salts used in these experiments had been purified to a point where their potentiometric titration with alkali was indistinguishable from that of potassium chloride.

Following exchange the solutions were neutralized with concentrated hydriodic acid and evaporated to dryness *in vacuo*. The residues were leached with acetone to remove sodium iodide and recrystallized from absolute ethanol. In all cases but the tetramethylarsonium iodide (m.p. 323-326° with dec.) the salts had the same m.p. as the starting material. The salts were dried over phosphorus pentoxide for 5 hr. at 100° *in vacuo* before combustion.

The exchange of bicyclo[2.2.1]heptane-1-sulfonium iodide (see Table I) was initially 1.0 *M* in salt and 0.3134 *M* in sodium deuterioxide. An insoluble oil formed and the concentration of deuterioxide ion dropped to 0.2078 *M*. Following centrifugation the aqueous solution was neutralized with concentrated hydriodic acid and evaporated *in vacuo*. The residue was leached several times with acetone and recrystallized from ethanol.

Dried butyl sulfoxide (1.0 g., 0.006 mole) in 5 cc. of 2.215 *M* sodium deuterioxide solution was heated at 56° for 120 hr. About 1/2 of the butyl sulfoxide dissolved. The mixtures were shaken frequently, and at the end of the runs the

cooled solutions were acidified with concentrated hydrochloric acid, centrifuged and the lower layers withdrawn. Following drying *in vacuo* the recovered butyl sulfoxide had m.p. 33.8°.

Kinetic Runs.—The solutions were prepared as described below from sodium deuterioxide-deuterium oxide solutions prepared as above. At the beginning and end of each run as well as throughout the runs when samples were removed, the concentration of deuterioxide ion was determined by several titrations with an Ultramicro Buret (Emil Greiner and Co., N. Y.). In no run had the concentration of deuterioxide decreased by more than 0.3% during the reaction. The samples were quenched with hydriodic acid, evaporated

TABLE V
DEUTERIUM EXCHANGE OF TRIMETHYLSULFONIUM (S⁺) AT 26.80°

Time, sec. × 10 ³	Deuterium exchange, N _D × 10 ²	log (1/(1 - N _D)) × 10 ²
0	1.162	5.365
4.605	2.427	12.07
7.515	3.080	15.99
11.245	3.906	21.50
14.925	4.297	24.39
$k' = 3.00 \pm 0.3 \times 10^{-5} \text{ sec.}^{-1}$		
0	1.223	5.663
4.560	2.457	12.24
7.530	3.114	16.20
11.230	3.908	21.52
14.890	4.404	25.21

$$k' = 3.06 \pm 0.05 \times 10^{-5} \text{ sec.}^{-1}$$

^a N_D is the atom fraction of deuterium.

to dryness, leached with acetone until colorless, recrystallized twice from absolute ethanol, and dried *in vacuo* over phosphorus pentoxide for at least 5 hr. at 100°. Typical data are shown in Table V. Five points were determined for each run. The pseudo first-order rate constants were calculated by least squares method and divided by the concentration of alkali to give the second-order rate constants reported in Table II. In the N⁺ case, the concentration of deuterioxide was corrected for solution expansion from 25 to 83.6°.

(a) P⁺.—A solution of P⁺ (0.6542 g., 0.003 mole) in sodium deuterioxide solution was diluted to 10.0 cc. with additional alkaline deuterium oxide. This solution, 0.2605 *M* in deuterioxide ion, was rapidly transferred to a 15-cc. centrifuge tube, sealed with a self-sealing stopper and maintained at 26.800 ± 0.002°.

A similar run, 0.2612 *M* in deuterioxide ion was maintained at 56.4 ± 0.1° in the Nujol-filled well of a constant temperature flask heated by refluxing acetone. A second exchange, 0.3 *M* in P⁺ but 0.3868 *M* in deuterioxide ion was also run at 56.4°.

(b) S⁺.—Two identical runs (Table V) were effected in which S⁺ (0.6122 g., 0.003 mole) in 10 cc. of solution, each solution being 0.2615 *M* in deuterioxide ion, was maintained at 26.800 ± 0.002°. A third run, identical in all respects, was maintained at 0.0 ± 0.1°.

(c) N⁺.—N⁺ (1.3752 g., 0.0068 mole) was stirred in 10 cc. of deuterium oxide with 1.62 g. (0.007 mole) of silver oxide till the supernatant gave a negative iodide test. Deuterium oxide, 12 cc., was added, stirred, filtered and the supernatant divided into two equal portions of roughly 10 cc. each. Each portion was placed into a stainless steel tube of 14 cc. capacity and sealed with rubber stoppers which had been boiled in potassium hydroxide solution. One tube was immersed to the lip in a stirred 5-gallon oil-bath kept at 83.6 ± 0.2°. The second tube, immersed in the well of a constant temperature flask filled with Nujol, was maintained at 100.0 ± 0.1° by refluxing water. At intervals, the 83° run was removed from the bath and cooled. A sample was removed and the tube was resealed with a fresh stopper to prevent evaporation of solvent. The 100° run was sealed with a self-sealing stopper so that sample removal could be effected by hypodermic syringe.

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(33) Mildred Cohn, "Preparation and Measurement of Isotopic Tracers," edited by J. W. Edwards, Ann Arbor, Mich., 1947, p. 51.

(34) Kindly prepared and analyzed by Professor D. Rittenberg of the College of Physicians and Surgeons, Columbia University, New York.