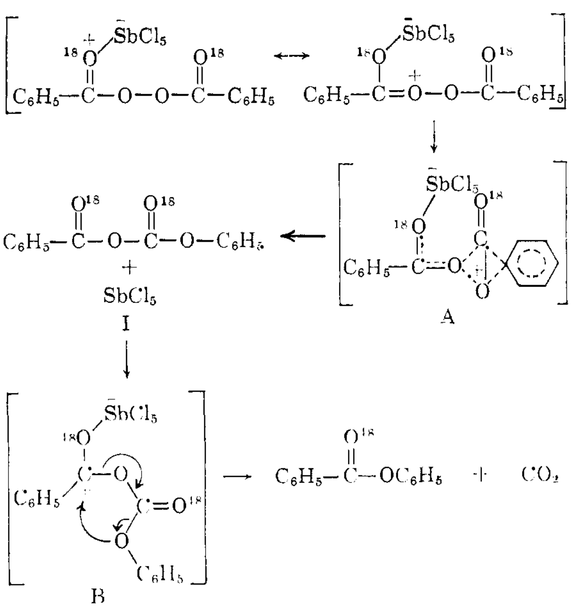

of antimony pentachloride suggest the mechanism shown. The first step involves a Lewis acid catalyzed carboxy inversion reaction which proceeds through transition state A to give the mixed carbonate, I.[3] This hypothesis is supported by the report of Rasuwajew, *et al.*,[3a] who have observed that antimony pentachloride catalyzed the rearrangement of acyl–sulfonyl peroxides to give mixed carbonates of an alkane sulfonic acid and phenol. The migration of phenyl to a peroxidic oxygen is in accord with a previous study of the carboxy inversion reaction.[3c] The complete retention of the label in the migrating benzoyloxy group is unique[3d] but accords with the postulate that antimony pentachloride is complexed with the carbonyl oxygen. The medium effects probably are due to interaction of the antimony pentachloride with the solvents.[4] Such interaction will inhibit complex formation with the peroxide and therefore diminish the rate of the reaction.

The mechanism postulates the formation of I, or an antimony pentachloride complex of I, as an intermediate. A sample of I[5] rapidly decomposed in petroleum ether in the presence of antimony pentachloride to give phenyl benzoate; no benzoic anhydride could be detected. Because of the inherent instability of I, ethyl benzoyl carbonate (II) was prepared. This material is stable at room temperature but decomposes at 150° to give ethyl benzoate, diethyl carbonate and benzoic anhydride.[6] Treatment of II in petroleum ether, at room temperature, with antimony pentachloride led to fairly rapid decomposition, *ca.* five hours. Carbon dioxide was evolved. Ethyl benzoate, contaminated with *ca.* 5% of benzoyl chloride, was the only product detected. No diethyl carbonate or benzoic anhydride could be found. A mixture of diethyl carbonate, benzoic anhydride and antimony pentachloride in petroleum ether did not give carbon dioxide or ethyl benzoate.

These results demonstrate that antimony pentachloride is a remarkably efficient catalyst for the decomposition of these mixed carbonates. Two possibilities present themselves for explaining the catalytic effect. The first suggests that antimony pentachloride acts as a phenoxide or ethoxide carrier and directs it to attack at only the benzoyl carbonyl. Such a chain of events seems highly improbable. The second, and more attractive, mechanism suggests that antimony pentachloride complexes with the benzoyl carbonyl and promotes intramolecular decomposition to give the products directly. This transformation is represented by B. A similar mechanism has been proposed by Boschan[7] to explain the decomposition of the mixed carbonate from trifluoroacetic acid and cholesterol. It should be noted that this postulate also explains the rate enhancing effect of boron trifluoride etherate on the decomposition of ethyl benzoyl carbonate.[6c]

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[3] (a) G. A. Rasuwajew, V. R. Likhterow and V. S. Etlis, *Tetrahedron Letters*, No. 15, 527 (1961); (b) J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 67 (1950); (c) D. B. Denney, *ibid.*, **78**, 590 (1956); (d) D. B. Denney and D. G. Denney, *ibid.*, **79**, 4806 (1957).

[4] H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willfang, *J. prakt. Chem.*, **154**, 112 (1940).

[5] The mixed carbonate was prepared from phenyl chloroformate and benzoic acid in the presence of triethylamine. It decomposes at room temperature to give phenyl benzoate, carbon dioxide, benzoic anhydride and presumably diphenyl carbonate. Freshly prepared material had m.p. 55–58° dec. The infrared spectrum had carbonyl bands at 5.45 and 5.65 μ.

[6] (a) E. T. Longosz and D. S. Tarbell, *J. Org. Chem.*, **26**, 2161 (1961). (b) D. S. Tarbell and E. T. Longosz, *ibid.*, **24**, 774 (1959); (c) T. Windholz, *ibid.*, **25**, 1703 (1960).

[7] R. Boschan, *J. Am. Chem. Soc.*, **81**, 3341 (1959).

CATALYSIS BY SECONDARY VALENCE FORCES[1]

Sir:

The second-order reaction of phenoxide ion with benzyldimethylsulfonium ion in water at 80° appears to be *accelerated* by ancillary molecular bonding of the π-complex or charge transfer type[2] at the transition state.

The rate constant for 0.12 M sodium phenoxide with 0.08 M benzyldimethylsulfonium p-toluenesulfonate is $2.7 \times 10^{-4}\ M^{-1}$ sec.$^{-1}$ in water at 79.8°. For the stronger base sodium hydroxide instead of sodium phenoxide, it is only $8.1 \times 10^{-5}\ M^{-1}$ sec.$^{-1}$. Gas chromatography on ether extracts indicates that benzyl phenyl ether is formed in 89% yield from the first reaction under kinetic conditions, and benzyl alcohol in 93% from the second. On the other hand, hydroxide is 1.50 times as reactive as phenoxide with methyl bromide in water at 25°.[3] With trimethylsulfonium perchlorate in water at 79.8°, another case where π-complexing is impossible, hydroxide ($3.6 \times 10^{-6}\ M^{-1}$ sec.$^{-1}$)

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[1] Supported in part by the Atomic Energy Commission and by NSF and NIH predoctoral fellowship to L. J. T.

[2] M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949, pp. 18, 184; R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952); L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954); H. G. Smith and R. E. Rundle, *J. Am. Chem. Soc.*, **80**, 5075 (1958).

[3] J. J. Bloomfield, Ph. D. Thesis, M.I.T., September, 1958, pp. 14, 15.

TABLE I

ACTIVATION PARAMETERS FOR REACTIONS OF PHENOXIDE AND HYDROXIDE IONS WITH SULFONIUM IONS[a]

Reactants	ΔF^* at 80°, kcal. mole^{-1}	ΔH^*, kcal. mole^{-1}	ΔS^*, e.u.
$C_6H_5O^- + C_6H_5CH_2S(CH_3)_2^+$	26.5	25.0	−4.4
$HO^- + C_6H_5CH_2S(CH_3)_2^+$	27.4	25.9	−4.3
$C_6H_5O^- + (CH_3)_3S^+$	30.1	28.5	−4.6
$HO^- + (CH_3)_3S^+$	29.6	26.8	−7.9

[a] 60–80° for $C_6H_5CH_2S(CH_3)_2^+$, 80–100° for $(CH_3)_3S^+$.

is again more reactive than phenoxide (1.7×10^{-6} M^{-1} sec.$^{-1}$). Heats and entropies are listed in Table I.

No π-complexing was detected between the initial reactants in solution. No maximum was observed in the ultraviolet or visible spectrum above 305 mμ with 0.12 *M* phenoxide and 0.08 *M* benzyldimethylsulfonium ion in 0.1 mm. cells. The region below 305 mμ was obscured by strong absorptions characteristic of the separate reactants.

Ross and Kuntz found that molecular complex formation *retarded* the reaction of aniline with 1-chloro-2,4-dinitrobenzene.[4] Perhaps the initial-state complexing is stronger than the extra interaction in the transition state because amino and nitro groups are closer together. On the other hand, π-complexing between phenoxide and benzyldimethylsulfonium ions might be expected to be stronger at the transition state, where the reactants are already bonded by one O---C bond and necessarily in close proximity.

Our results have no bearing on the question of whether a π-complex distinct from the transition state may be a discrete intermediate in the reaction.

[4] S. D. Ross and J. Kuntz, *J. Am. Chem. Soc.*, **76**, 3000 (1954).

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RECEIVED APRIL 10, 1962

STRUCTURE OF DIMETHYL PHOSPHINOBORINE TETRAMER

Sir:

The trimer and the tetramer of $(CH_3)_2PBH_2$ have been prepared by Burg.[1] They exhibit unusual stability. It has been suggested that this stability of the boron–phosphorus bond arises in large part from the availability of *d* orbitals on the phosphorus atoms. The deviation of the B–P–B angle from a tetrahedral value in the structure of the trimer determined by Hamilton seems to support such a view.[2] Similar results now have been obtained for $[(CH_3)_2PBH_2]_4$ by single crystal X-ray diffraction.

The tetramer crystallizes in the monoclinic space group Cc with four molecules per unit cell. The unit cell parameters are $a = 21.49$, $b = 6.04$, $c = 17.89$ Å. and $\beta = 125° 24'$.

The coördinates of the phosphorus atoms were found from Patterson projections by hand-superposition techniques. Use of these positions in conjunction with *hkl* data to construct a three-dimensional electron density map gave the coördinates of the remaining atoms. The hydrogen positions are still to be determined.

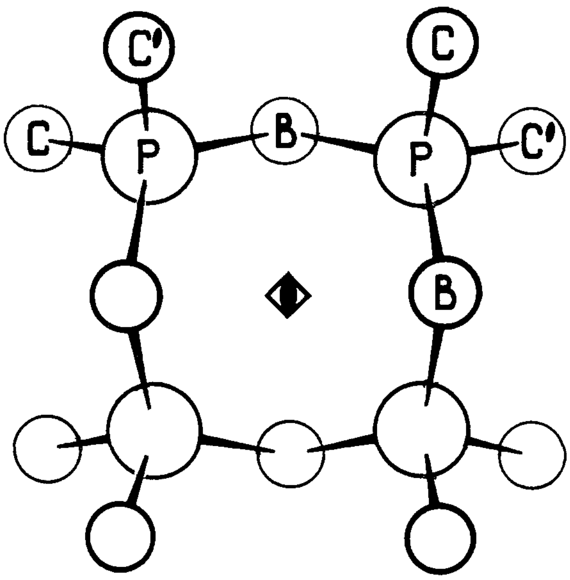

Figure 1.

The molecule consists of an eight-membered ring with alternating boron and phosphorus atoms and two methyl groups on each phosphorus. The ring itself is puckered and exhibits D_{2d} symmetry (Fig. 1). At the present stage of refinement, with all atoms except hydrogen included, the agreement factor $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$ is 0.18 for 528 observed reflections. Further refinement is still in progress on the CDC 1604 computer. Present values for some of the average bond angles and distances are B–P–B = 125 ± 1, P–B–P = 104 ± 2, C–P–C = 103 ± 2°; P–B = 2.08 ± 0.05, P–C = 1.84 ± 0.04 Å.

We wish to thank Dr. A. B. Burg for supplying us with samples of the tetramer and the Army Research Office for financial aid in the investigation. We are also indebted to the National Science Foundation for a fellowship to Paul Goldstein.

[1] A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

[2] W. C. Hamilton, *Acta Cryst.*, **8**, 199 (1955).

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RECEIVED MAY 16, 1962

MOLECULAR WEIGHT OF VIRUS BY EQUILIBRIUM ULTRACENTRIFUGATION

Sir:

In the past, viruses, because of their high molecular weight (5×10^6 to 50×10^6), have not been studied by the standard equilibrium method. Since a value for the molecular weight, *M*, in the equilibrium sedimentation equation[1]

$$M = \frac{2RT \ln (f_2c_2/f_1c_1)}{(1 - \bar{v}\rho)4\pi^2N^2(x_2^2 - x_1^2)}$$

is inversely proportional to the square of the angular velocity, $4\pi^2N^2$, where *N* is the number of

[1] T. Svedberg and K. O. Pedersen, "The Ultracentrifuge," Oxford University Press, New York, N. Y., 1940, p. 51.