tion. These experimental results suggest that the ellipticity does not arise from vibronic coupling. The vibronic mechanism was also ruled out by Sugano[9] using symmetry arguments.

Data are available for other complexes and these data are consistent with the above interpretation. The use of ellipticity data in the analysis of optical rotatory dispersion curves of coördination compounds will be developed in more detailed publications.

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DEPARTMENT OF CHEMISTRY JOHN G. BRUSHMILLER
UNIVERSITY OF PITTSBURGH E. L. AMMA
PITTSBURGH 13, PENNSYLVANIA BODIE E. DOUGLAS

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THERMAL DECOMPOSITION KINETICS OF CARBON SUBOXIDE[1]

Sir:

Recently, Bayes[2] has reported on some experiments in which carbon suboxide, C_3O_2, was photolyzed with 2537 Å. radiation in the presence of added hydrocarbons. He suggests that the primary act is C–C bond breakage: $C_3O_2 \rightarrow C_2O + CO$. We wish to report some results for the pyrolysis of C_3O_2 which appear to have bearing on this question.

The pyrolysis has been performed with an annular flow system into which C_3O_2 is carried by a large excess of helium. The C_3O_2 is prepared by the method of Stock and Stoltzenburg,[3] with slight modification, and is stored at −80° or lower to avoid polymerization. Its infrared spectrum is essentially identical with that reported by Long, Murfin and Williams,[4] but it shows two additional bands reported by Lord and Wright[5] that probably are attributable to use of a higher concentration and longer path length than those employed by Long, *et al.* No bands are present that can be attributed to impurities.

The rate of decomposition of C_3O_2 is measured by following the deposition of film carbon on a specified length of the glazed porcelain rod that forms the inner boundary of the annular flow system. In another publication[6] we have described in detail the mathematical analysis by means of which the carbon deposition rate is related to the rate of disappearance of C_3O_2 in the gas phase.

C_3O_2 decomposition was studied between 900 and 1025°K. at 1 atmosphere total pressure. Concentrations of C_3O_2 ranged between about 0.1 and 0.5 mole per cent. in the helium. The effluent gas from the reactor contained only He, CO, and unreacted C_3O_2, as analyzed by means of a Beckman GC-1 chromatograph. Studies in a static system confirm that the stoichiometry of the decomposition at these temperatures is essentially $C_3O_2 \rightarrow C(s) + 2CO$.

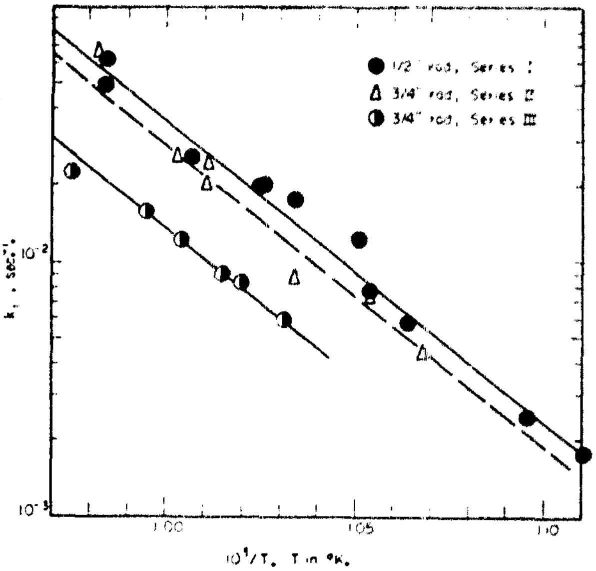

Fig. 1.

The gas-phase rate constant results for three series of runs are presented as an Arrhenius plot in Fig. 1. The slopes are quite well defined and yield an activation energy of 54 kcal., with an uncertainty of about ± 2 kcal. The range of experimental frequency factors is from 7.7×10^{14} cc./mole sec. to 2.05×10^{15} cc./mole sec., for an assumed second-order reaction. The reaction was proved first-order in $[C_3O_2]$ by variation of the suboxide concentration; however, we do not know the order in helium. The variation in the experimental frequency factor from series to series is perhaps attributable to differences in the flow characteristics, caused by minor differences in surface configurations of the three central rods employed. Agreement between Series I and Series II lends weight to the higher value for the frequency factor.

Unless decomposition of C_2O on the surface to give C(s) and CO is very slow, the 54 kcal. figure is almost certainly the activation energy for $C_3O_2 \rightarrow C_2O + CO$. A rough estimate of the ΔH for the only alternative gas-phase reaction, the splitting off of an O atom, puts it at some 183 kcal. endothermic.

By drawing analogies between polyatomic carbon molecules and the oxides of carbon (except CO), as Pitzer and Clementi have done,[7] we have estimated the ΔH of the primary reaction to be 46 ± 10 kcal./mole. In making these estimates, the figure −8.3 kcal./mole has been used for the heat of formation of gaseous C_3O_2.[8]

The estimates plus the experimental activation energy indicate that the back reaction between CO and C_2O has a probable activation energy on the order of 8 kcal., but with large uncertainty. They also indicate that the reaction $C_2O \rightarrow C(g) + CO$ is about 79 kcal. endothermic. Thus Bayes' suggestion that this reaction is occurring thermally at a rapid rate in his system seems to us an unlikely possibility. On the other hand, 2537 Å. photolysis

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(1) Work supported by the U. S. Atomic Energy Commission under contract AT(30-1)-1710.

(2) K. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961).

(3) A. Stock and H. Stoltzenburg, *Ber.*, **50**, 498 (1917).

(4) D. A. Long, F. S. Murfin, and R. L. Williams, *Proc. Roy. Soc.* (*London*), **A222**, 251 (1954).

(5) R. C. Lord and N. Wright, *J. Chem. Phys.*, **5**, 642 (1937).

(6) T. J. Hirt and H. B. Palmer, "Proceedings of the Fifth Conference on Carbon," Pergamon Press, New York, in press.

(7) K. S. Pitzer and E. Clementi, *J. Am. Chem. Soc.*, **81**, 4477 (1959).

(8) This figure is an estimate from the JANAF Interim Thermochemical Tables (Dow Chemical Company), communicated to us by Dr. C. H. Shomate, U.S.N.O.T.S., China Lake, Calif.

of C_2O to yield C and CO seems very probable, since it may well absorb strongly there even though ketene does not. Carbon suboxide itself, which may be a stronger analog to C_2O than is ketene, does absorb strongly in this region.

DEPARTMENT OF FUEL TECHNOLOGY
COLLEGE OF MINERAL INDUSTRIES H. B. PALMER
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA T. J. HIRT

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SELECTIVITY IN SOLVOLYSES CATALYZED BY POLY-(4-VINYLPYRIDINE)[1]

Sir:

Selectivity in enzymatic reactions apparently arises from the preferential binding, by electrostatic or secondary valence forces, of the substrate to the catalyst prior to the covalent changes in the substrate. As a simple model[2] for an enzyme system we chose for study poly-(4-vinylpyridine). In weakly acidic solutions this polymer would possess both cationic sites, which by electrostatic attraction should bind anionic substrates to the polymer,[3] and basic nitrogen atoms, which in low molecular weight compounds are known to catalyze the hydrolysis of nitrophenyl esters.[4] 2,4-Dinitrophenyl acetate (DNPA) and potassium 3-nitro-4-acetoxybenzenesulfonate (NABS) were employed as substrates, the former to illustrate the behavior of an uncharged substrate and the latter to reveal the effect of charge interaction between a poly-ion and a substrate counter ion on the course of a catalyzed solvolysis. For comparison purposes solvolyses catalyzed by 4-picoline, a model for the repeating unit of the polymer, also were examined.

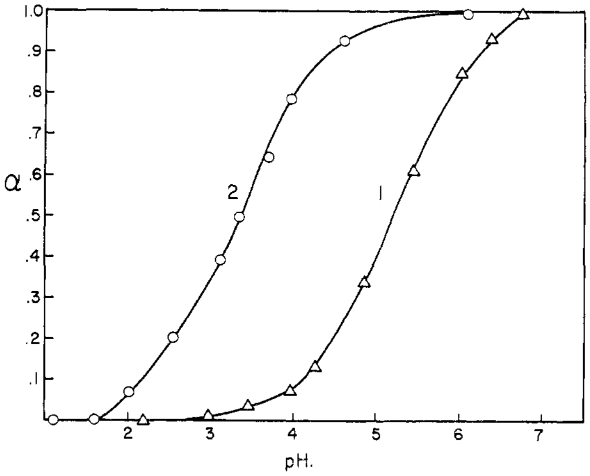

Fig. 1.—Titration curves for 4-picoline, Δ (curve 1), and poly-(4-vinylpyridine), O (curve 2), in 50% (v./v.) ethanol–water, 0.04 M in KCl at 36.6°.

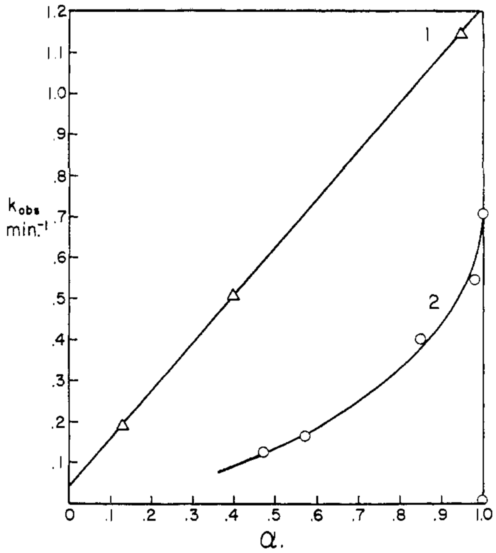

Fig. 2.—Solvolysis of 2,4-dinitrophenyl acetate catalyzed by 0.0157 M 4-picoline, Δ (curve 1), and by 0.010 base molar poly-(4-vinylpyridine), O (curve 2).

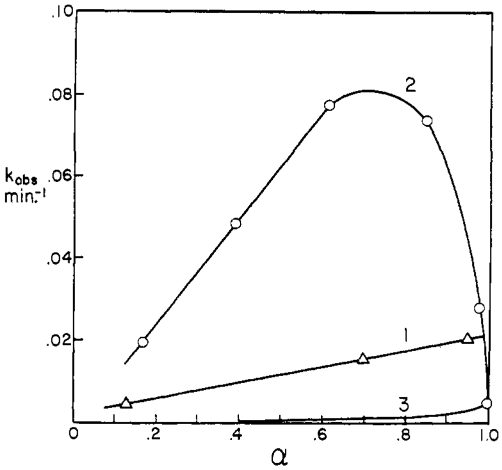

Fig. 3.—Solvolysis of potassium 3-nitro-4-acetoxybenzenesulfonate catalyzed by 0.0157 M 4-picoline, Δ (curve 1) and by 0.010 base molar poly-(4-vinylpyridine), O curve 2.

The reactions were carried out at 36.6° in 50% (v./v.) ethanol–water which was 0.04 M in potas-

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[1] This research was supported in part by a grant from the National Science Foundation, G7414.

[2] J. R. Whitaker and F. E. Deatherage, *J. Am. Chem. Soc.*, **77**, 3360, 5298 (1955), found that glycylcycine hydrolyzed faster than acetylglycine with Dowex-50 as a catalyst but more slowly than acetylglycine in hydrochloric acid solution. The Dowex resin was insoluble in water and it may be assumed that the basic peptide was preferentially held in the acid medium within the resin particles. Attempts to attain selectivity with homogeneous catalysts have been less successful. M. L. Bender and Y. L. Chow, *ibid.*, **81**, 3929 (1959), observed that the 2-aminopyridinium ion appeared to be unusually effective as a catalyst in the hydrolysis of o-nitrophenyl oxalate anion. The result could be ascribed to "electrostatic catalysis"; however, as pointed out by Bender, an ambiguity exists in the interpretation of this experiment for a reaction of the nitrophenyl oxalate anion with the aminopyridinium ion cannot be distinguished kinetically from a reaction of nitrophenyl hydrogen oxalate with 2-aminopyridine.

[3] Numerous studies of counter ion binding by polyelectrolytes have been reported. See for example, F. T. Wall and W. B. Hill, *J. Am. Chem. Soc.*, **82**, 5599 (1960); F. T. Wall and M. J. Eitel, *ibid.*, **79**, 1550, 1556 (1957); I. Kagawa and K. Katsuura, *J. Poly Sci.*, **17**, 365 (1955); H. P. Gregor and D. H. Gold, *J. Phys. Chem.*, **61**, 1347 (1957); P. Doty and G. Ehrlich, *Ann. Rev. Phys. Chem.*, III (1952). It is noteworthy that H. Ladenheim, E. M. Loebl, and H. Morawetz, *J. Am. Chem. Soc.*, **81**, 20 (1959), found that poly-(4-vinylpyridine) functioned selectively in a non-catalytic reaction, the quaternization with α-bromoacetamide and with bromoacetate ion.

[4] See M. L. Bender, *Chem. Rev.*, **60**, 53 (1960), for a review of hydrolytic reactions catalyzed by pyridine, imidazole, and related nucleophiles.