

THE KINETICS OF CYCLOPENTADIENE

Sir:

In a recent letter in *Nature*, 137, 496-7 (1936), Wasserman and Khambata discuss the rates of polymerization of cyclopentadiene and of the depolymerization of dicyclopentadiene in solution. Since we have studied these reactions for some time, we wish to report our results which, in several instances, are more extensive than those of Wasserman. In the gas phase the reactions were found to be of the second and of the first order, respectively. Their velocity constants are given by

$$\text{Polymerization } k = 6.5 \times 10^6 e^{-12,700/RT} \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$

$$\text{Depolymerization } k = 10^{12} e^{-33,700/RT} \text{ sec.}^{-1}$$

While the constants in these expressions differ somewhat from those given by Wasserman and Khambata, the absolute rates are nearly the same, indicating that the differences are mostly to be attributed to experimental errors in determining the temperature coefficients of the rates. We have also studied the association reaction in tetrahydronaphthalene as solvent, and find, as did Wasserman, that the reaction is of the second order.

We also find, however, that with pure liquid cyclopentadiene the order decreases, a reaction of nearly first order obtaining while the activation energy (17,300 kcal.) is still practically identical with that found by Wasserman.

TABLE I
DIMERIZATION OF PURE LIQUID CYCLOPENTADIENE,
58.4°

Time, sec.	Mole % cyclo- pentadiene	k (1st order)	k (2nd order)
0	98.9		
1215	87.4	9.8×10^{-5}	1.09×10^{-7}
4830	61.3	9.8	1.34
12640	28.8	9.6	2.43

Earlier work on this reaction and our own experiments definitely show that no chains are involved and thus the change of the reaction order must be attributed to other causes. While their discussion is reserved for the more detailed publication soon to follow, we wish to point out that this finding may have a very important bearing on the kinetics of other, more complex, polymerization reactions in pure liquids. Rideal and Gee [*Trans. Faraday Soc.*, 31, 969 (1935)] and Mark and Dostal [*Z. physik. Chem.*, 29B, 299 (1935)] recently have discussed the mechanism of such reactions, deriving kinetic expressions which account for the first order in terms of the chain

mechanism. If, as we now find, the first order is due not to the intervention of the chains but to the changing environment during the progress of the reaction, these kinetics interpretations, when applied to pure liquid reactants, should be considerably revised.

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THE LUCIFERIN-OXYLUCIFERIN SYSTEM

Sir:

By connecting solutions of a series of partially reduced oxidation-reduction indicators with crude extracts of oxyluciferin, both the solutions and extracts being oxygen-free and buffered at the same pH, through platinum electrodes and a salt-bridge, I have found that the oxidation-reduction potential of luciferin-oxyluciferin lies in the neighborhood of the quinhydrone system. (The oxyluciferin was obtained by extracting powdered *Cypridina* with the phosphate buffer, filtering and allowing to stand until all luminescence had ceased due to complete oxidation of the luciferin. Reduction of the oxyluciferin to luciferin was indicated by appearance of luminescence when air was passed through the extract.) Although it has hitherto been thought that there is a gap of about 0.5 v. in oxidation-reduction potential between the systems which reduce oxyluciferin and those which oxidize luciferin upon mixing (quinhydrone representing the level at which luciferin is oxidized) I have now found, in addition to the above evidence, that the system is reversible, since if a luciferin extract is connected in the above manner with an oxyluciferin extract, some of the latter is reduced to luciferin. The amount of reduction in all cases was, however, small, due to the instability of oxyluciferin, as shown by Harvey and by Anderson.

To the facts that (1) luciferin is slowly autooxidized in the physiological pH range, that (2) its oxidation by oxygen is catalyzed by an enzyme (luciferase) and that (3) the oxidant is unstable, may now be added the facts that (4) the system is at least partially reversible, (5) is active at an electrode and (6) has, for a biological compound, an unusually positive oxidation-reduction potential. It is noteworthy that these characteristics are similar to those of a group of substances in which certain special derivatives of ortho- and