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

$$\text{Polymerization } k = 6.5 \times 10^{6}\, e^{-12{,}700/RT} \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$
$$\text{Depolymerization } k = 10^{13}\, e^{-33{,}700/RT} \text{ sec.}^{-1}$$

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 % cyclopentadiene	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.

MALLINCKRODT CHEMICAL LABORATORY
HARVARD UNIVERSITY G. B. KISTIAKOWSKY
CAMBRIDGE, MASSACHUSETTS WHITNEY H. MEARS

RECEIVED MAY 15, 1936

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 *p*H, 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 autoxidized in the physiological *p*H 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 para-hydroxybenzenes are the reductants and some representatives of which have been investigated by Ball and Chen, *e. g.*, epinephrine, catechol, pyrogallol and gallic acid.

I should like, also, to suggest, from a consideration of the available facts, that luciferase serves the same oxidative function with regard to luciferin as oxidases such as catechol oxidase, laccase, and polyphenolase do, to their respective substrates.

THE PHYSIOLOGICAL LABORATORY
PRINCETON UNIVERSITY
PRINCETON, N. J.
IRVIN M. KORR

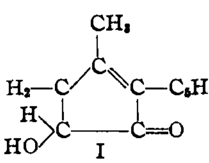
RECEIVED MAY 13, 1936

CONSTITUENTS OF PYRETHRUM FLOWERS. V. CONCERNING THE STRUCTURE OF PYRETHROLONE

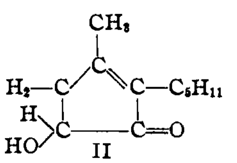
Sir:

In article IV of this series [*J. Org. Chem.*, **1**, 38 (1936)] we have reported that the semicarbazones of pyrethrolone and tetrahydropyrethrolone contain two less hydrogen atoms than are required by their accepted formulas. Pyrethrolone semicarbazone corresponds to the formula $C_{12}H_{17}O_2N_3$ and tetrahydropyrethrolone semicarbazone to $C_{12}H_{21}O_2N_3$. The formulas for pyrethrolone and tetrahydropyrethrolone would therefore be represented by $C_{11}H_{14}O_2$ and $C_{11}H_{18}O_2$, respectively. These formulas have now been confirmed by analyses of the free ketones and some of their derivatives.

The establishment of the new empirical formulas for pyrethrolone and tetrahydropyrethrolone necessitates a revision of their structural formulas, and we suggest that formulas I and II be assigned to pyrethrolone and tetrahydropyrethrolone, respectively.

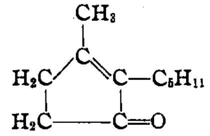


I



II

Tetrahydropyrethrolone, having a saturated side chain, is better suited for study of the nuclear reactions than is pyrethrolone. The hydroxyl group is readily replaced by chlorine, and the resulting chloro derivative yields on reduction an optically inactive ketone of probable structure III. This formula, on the basis of degradation and synthesis, has been assigned to dihydrojasmone, the semicarbazone of which melts at 175°. The semicarbazone of our reduced compound melts at 176°. While it has not been possible to make a mixed melting point, the two values are so close as to indicate identity [Treff and Werner, *Ber.*, **66**, 1521 (1933); Staudinger and Ruzicka, *Helv. Chim. Acta*, **7**, 257 (1924)].



III

With the assumption that tetrahydropyrethrolone corresponds to formula II, its recorded characteristic reactions also are readily explained.

DIVISION OF INSECTICIDE INVESTIGATIONS
BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.
F. B. LAFORGE
H. L. HALLER

RECEIVED MAY 21, 1936

THE CONSTANCY OF NUCLEAR BOND ENERGIES

Sir:

Recent accurate determinations of the masses of the lighter elements [Oliphant, *Nature*, **137**, 396 (1936)] permit a further check on the assumption [Latimer and Libby, *J. Chem. Phys.*, **1**, 133 (1933)] that the energies of nuclear reactions can be calculated as the sum of changes in the energies of the nuclear bonds and the coulombic fields. As an approximation for the latter, Latimer and Libby used the classical expression $M_F = 2Z^2/3R$, where Z is the charge and R the radius. Experimental values for the nuclear radii agree very well with the equation [Dunning, *Phys. Rev.*, **45**, 587 (1934)] $R = 1.315 \times 10^{-13} \sqrt[3]{\text{at. wt.}}$ Using these values for the radii we may calculate M_F for each nucleus and the ΔM_F for nuclear reactions. The difference between the experimental change in mass, ΔM, and the ΔM_F then constitutes a measure of the change in the nuclear bond energies.

In Table I the data expressed in atomic weight units are summarized for reactions involving the emission of positrons and electrons. For the positron reactions the bond calculated is remarkably constant and appears to be simply the energy of the reaction: neutron plus positron to give a proton. For the five electron reactions, however, the energy for the conversion of a neutron to a proton is considerably smaller than the energies of the other four reactions, so that the bond energy must represent the expulsion of an electron from a H^4 group to form He^4.