centrations and excess of acid present may be entirely or almost entirely controlled by the chemical rate; in such solutions the copper surface remains very bright with no trace of oxide film. On the other hand, in solutions of low acid and high peroxide concentration, the rate may have an entirely new significance because of surface coatings which partly prevent access of reagents to the copper itself.

Summary

The rate of solution of polycrystalline copper from a rotating cylinder has been measured, in solutions of acetic acid and various oxidizing agents, especially hydrogen peroxide and quinone; and in solutions of ferric chloride and nitrate, with the addition of hydrochloric acid.

From the temperature coefficient, variation in rate with rotational speed, effect of changed viscosity and a comparison of the rate with that of other metals dissolving in acid solutions, it has been concluded that the rate in the ferric salt solutions is largely diffusion-controlled. In the acetic acid solutions, the rate may be entirely or partly controlled by the rate of the chemical reation; in some of these solutions surface coatings may mechanically prevent access of reagent to the copper surface or otherwise change the character of the reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

The Mechanism of the Decomposition of Ethylene Iodide

BY RICHARD A. OGG, JR.

The thermal homogeneous decomposition of gaseous ethylene iodide was found by Arnold and Kistiakowsky[1] to obey the rate expression

$$-\mathrm{d}(\mathrm{C_2H_4I_2})/\mathrm{d}t = k_1(\mathrm{C_2H_4I_2}) + k_2(\mathrm{I_2})^{1/2}(\mathrm{C_2H_4I_2})$$

The first term on the right was interpreted by these investigators to indicate a dissociation in one act (into ethylene and iodine) of the ethylene iodide molecule. The author wishes to show that this is not necessarily the case, and that the chain mechanism postulated to account for the second term may be extended to account entirely for the whole rate expression.

The following steps are considered, with corresponding rate constants. The heat effects, whose estimation is described below, are given in kilogram calories per mole

(a)	$\mathrm{C_2H_4I_2} \longrightarrow \mathrm{C_2H_4I} + \mathrm{I}$	−36.6	k_a
(b)	$\mathrm{I_2} \rightleftarrows 2\mathrm{I}$ (Equilibrium)	−36.6	K_{I_2}
(c)	$\mathrm{C_2H_4I_2} + \mathrm{I} \longrightarrow \mathrm{C_2H_4I} + \mathrm{I_2}$	± 0	k_c
(d)	$\mathrm{C_2H_4I} + \mathrm{I_2} \longrightarrow \mathrm{C_2H_4I_2} + \mathrm{I}$	± 0	k_d
(e)	$\mathrm{C_2H_4I} \longrightarrow \mathrm{C_2H_4} + \mathrm{I}$	−13.4	k_e

This set of processes is very similar to that proposed for the decomposition of *s*-butyl iodide.[2]

The rate expression derived from the above steps is

$$\frac{-\mathrm{d}(\mathrm{C_2H_4I_2})}{\mathrm{d}t} = \frac{k_a(\mathrm{C_2H_4I_2}) + K_{I_2}{}^{1/2}k_c(\mathrm{I_2})^{1/2}(\mathrm{C_2H_4I_2})}{k_d/k_e\,(\mathrm{I_2}) + 1}$$

This reduces to the experimental expression, with $k_a = k_1$ and $K_{I_2}{}^{1/2}k_c = k_2$ if the quantity $k_d/k_e\,(\mathrm{I_2})$ is negligible in comparison with unity. Estimation of the absolute magnitudes of k_d and k_e shows this to be the case.

The heat effect of reaction (a) is taken as the activation energy for the unimolecular dissociation[2,3] which is identified with the activation energy found by Arnold and Kistiakowsky for the rate constant k_1 (since $k_1 = k_a$). The value 36.6 kilocalories per mole is about that to be expected, since the carbon–iodine bond strength in methyl, ethyl and *n*-propyl iodides[3] is some 43 kilocalories per mole, and that in *s*-butyl iodide[2] 39.5 kilocalories per mole.

The heat of dissociation of gaseous iodine in the temperature region concerned (some 200°) is obtained from the data of Bodenstein and Starck.[4] The remaining heats of reaction are obtained by Hess's law, using in addition the value −13.4 kilocalories per mole found by Cuthbertson and Kistiakowsky[5] for the gas phase reaction $\mathrm{C_2H_4I_2} \longrightarrow \mathrm{C_2H_4} + \mathrm{I_2}$.

At the highest temperature in their study (230°) Arnold and Kistiakowsky found that the rate constant k_2 to have the value 12.75 (mole/cc.)$^{-1/2}$ sec.$^{-1}$. At this temperature K_{I_2} (the dissociation

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[1] L. Arnold and G. B. Kistiakowsky, *J. Chem. Phys.*, **1**, 166 (1933).

[2] R. A. Ogg, Jr., and M. Polanyi, *Trans. Faraday Soc.*, **31**, 482 (1935).

[3] R. A. Ogg, Jr., THIS JOURNAL, **56**, 526 (1934).

[4] M. Bodenstein and H. Starck, *Z. Elektrochem.*, **16**, 961 (1910).

[5] G. R. Cuthbertson and G. B. Kistiakowsky, *J. Chem. Phys.*, **3**, 631 (1935).

constant[4] of I_2) is 7.71×10^{-16} mole/cc. Hence $k_c(=k_2/K_{I_2}^{1/2})$ has the value 4.5×10^8 (mole/cc.)$^{-1}$ sec.$^{-1}$. These investigators gave 30.2 kilocalories per mole as the activation energy for k_2. Subtracting one-half of the heat of dissociation of I_2, one finds 11.9 kilocalories per mole as the activation energy of reaction (c).

Since (c) is thermoneutral, the activation energy of the opposed reaction (d) is the same as for (c). Therefore no serious error is made if k_d is assumed approximately equal to k_c. Hence at 230° k_d is some 4.6×10^8 (mole/cc.)$^{-1}$ sec.$^{-1}$.

The rate constant k_e is assumed to be given by the expression $10^{13}e^{-Q/RT}$ sec.$^{-1}$, which holds approximately for a large number of unimolecular reactions. The activation energy is taken as the heat effect of (e), *i. e.*, 13,400 calories per mole. Hence at 230° k_e is 1.6×10^7 sec.$^{-1}$.

The *highest* concentration of iodine in the experiments of Arnold and Kistiakowsky was some 100–150 mm., *i. e.*, of the order of 5×10^{-6} mole/cc. and was ordinarily much smaller. At 230° the *largest* value of k_d/k_e (I_2) was some 1.4×10^{-4}, which is negligible in comparison with unity, as stated above. At lower temperatures this is also true, since k_d and k_e have nearly equal temperature coefficients. Even were the value of k_e to be some five-hundred fold smaller than the above estimate, corresponding to an increase in activation energy of over five kilocalories per mole, k_d/k_e (I_2) would still be negligible. One may conclude that under the experimental conditions of Arnold and Kistiakowsky reaction (d) plays no appreciable role, and that the above mechanism is in entire agreement with the experimental rate expression.

Reaction (d), a metathesis involving a free radical, is seen to have a *true* activation energy of some 11.9 kilocalories per mole. This agrees rather closely with the true activation energy of 14.2 kilocalories per mole for the reaction of *s*-butyl radicals[2] with iodine molecules, and furnishes another example of the surprising inertia of reactions of free radicals.

The above discussion indicates that despite the simple first order rate expression for the *uncatalyzed* decomposition of ethylene iodide, the corresponding reaction may occur in two consecutive steps. The same applies of course to the addition of iodine to ethylene. The fact that the iodine-sensitized reaction has a rate comparable to the unsensitized process is rather fortuitous, arising from the absolute magnitude of the true activation energy of (c). Were the true activation energy of (c) to be larger by a few kilocalories per mole, the sensitized reaction would be negligible, and the second term in the rate expression would disappear, leaving the reaction apparently simple first order, despite its actual chain character.

An example of the situation discussed in the preceding paragraph appears to be offered by the decomposition and synthesis of allyl alcohol diiodide in solution.[6] These reactions appear to be simple first and second order, respectively. Again, it is unnecessary to assume addition or removal of the iodine molecule in one act. It is considered that a chain mechanism analogous to that for ethylene iodide obtains in this case, but that due to a somewhat greater activation energy for the analog of (c), the principal role in the decomposition is played by the analog of (a) followed by that of (e). Indication of the actual chain character of the reactions is found in their enormous acceleration by visible light (which produces iodine atoms by photodissociation).

Finally, the remarkable results of Bauer and Daniels[7] on the photo-addition of bromine to cinnamic acid may be interpreted in light of the above discussion. These authors found the quantum efficiency to approach *unity* at vanishingly small bromine concentrations. Their chain mechanism, invoking reactions analogous to (e) and its reverse and (d), led them to expect a limiting value of two for Φ. If the process analogous to the reverse of (a) be added, then at vanishing Br_2 concentration this should predominate over (d), and the chain reduces to the reverse of (e) followed by the reverse of (a). It is seen that this plausible process gives a limiting quantum efficiency of unity, and renders unnecessary the improbable energy chain proposed by Bauer and Daniels.

It is considered that there is no direct evidence necessarily indicating that addition to or removal from an ethylenic linkage of a halogen molecule ever occurs in a single act, and that such a process is a very improbable one. In gas phase or non-ionizing solvents a chain mechanism of the above type probably obtains. For reaction at a surface, or in ionizing solvents, the ionic chain mechanism suggested in a previous communication[8] may predominate.

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(6) F. G. Caughley and P. W. Robertson, *J. Chem. Soc.*, 1323 (1933).

(7) W. H. Bauer and F. Daniels, THIS JOURNAL, **56**, 378 (1934).

(8) R. A. Ogg, Jr., *ibid.*, **57**, 2727 (1935).

Summary

Consideration of the kinetic results on the decomposition of ethylene diiodide shows that a chain mechanism explains them completely. A similar conclusion is reached for the decomposition of allyl alcohol diiodide, and the photo-addition of bromine to cinnamic acid.

The proposal is made that the addition of halogens to an ethylenic linkage, or the corresponding reverse reaction need never occur in a single act.

STANFORD UNIVERSITY, CALIF.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

The Saponification and Thermal Decomposition of Mixed Diacyl Derivatives of 2-Amino-4-chlorothiophenol

BY HERMAN P. LANKELMA AND EDWARD VOPICKA

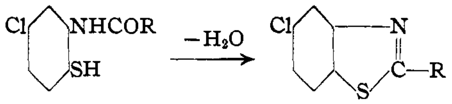
A study of mixed acyl derivatives of an *o*-aminophenol has shown that a migration of acyl between oxygen and nitrogen upon acylation, leading to identical mixed diacyl derivatives regardless of the order of introduction of the acyl radicals, is a general reaction. The acyl pair benzoyl–acetyl, for example, yield typical results in this respect.[1]

In a previous paper Lankelma and Knauf[2] have shown that when this acyl pair is employed with an *o*-aminothiophenol no migration of acyl occurred upon acylation, that is, an isomeric pair of mixed diacyl derivatives was obtained. Upon saponification of these mixed diacyl derivatives, however, the same monoacyl derivative, N-benzoyl, was obtained, showing that a migration of acyl between sulfur and nitrogen did occur upon saponification. The base employed in this work was 2-amino-4-chlorothiophenol.

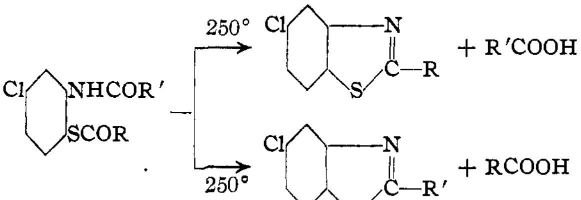
The present work, employing the same base, was undertaken to determine whether the behavior observed with the acyl pair benzoyl–acetyl was general where other pairs of acyl radicals were concerned. For this purpose the following four pairs of acyl radicals were employed: acetyl–phenylacetyl, acetyl–cinnamyl, benzoyl–cinnamyl, and benzoyl–phenylacetyl. Attempts to employ the propionyl radical were unsuccessful owing to the ease with which the mono-N-propionyl derivative lost water to form the corresponding benzothiazole.

It was found that with each of these four pairs of acyl radicals two isomeric diacyl derivatives were obtained, depending upon the order in which the acyl radicals were introduced. Also in each case saponification of the isomeric mixed diacyl derivatives gave the same mono-N-acyl derivative. Because of the ease with which these monoacyl derivative lose water to form the corresponding benzothiazole they are often difficult to purify.[2]

For this reason they were identified in this work in the form of the corresponding benzothiazoles.



It was also found that upon heating to a temperature of about 250° the diacyl derivatives were smoothly decomposed into the benzothiazole and the acid. In case a mixed diacyl derivative is subjected to this thermal decomposition it could yield two sets of products, depending upon the course of the cleavage.



Five isomeric pairs of mixed diacyl derivatives were decomposed in this way and in each case the pair in question gave a single set of products. The course of this cleavage therefore appears to be determined by the nature of the acyl radicals involved rather than by the element, sulfur or nitrogen, to which they are attached. It was also found that the benzothiazole obtained from a given isomeric pair of mixed diacyl derivatives by thermal decomposition was the same as that obtained by saponification at room temperature.

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(1) See papers by Raiford, THIS JOURNAL (1919-1926).

(2) Lankelma and Knauf, *ibid.*, 53, 309 (1931).