tion of carbon dioxide at the same percentage dehydration at temperatures of 34.5, 61.2 and 100°. This behavior is explained as due to the collapse of the crystal skeleton when the last fractions of the water are removed.

Slightly dehydrated chabasite exhibits a pronounced specificity of adsorption toward hydrogen, oxygen and carbon dioxide. This behavior is explained on the assumption of several limiting pore sizes and of differing extents of the corresponding inner surfaces.

CAMBRIDGE, MASS. RECEIVED AUGUST 19, 1936

# NOTES

## The Ethyl Esters of Triiodophenoxyacetic Acids and Potassium Triiodophenoxyacetate

BY T. C. DANIELS AND R. E. LYONS

Several hitherto undescribed triiodophenoxy substitution products of ethyl acetate have been prepared because of their possible opacity to x-rays. The procedure followed was similar to that used by Hewett, Johnson and Pope[1] in preparing tribromophenoxyacetic esters. A mixture of 0.05 mole of triiodophenol, with equivalent quantities of sodium and of ethyl mono-, di- or trichloroacetate, dissolved in 50 cc. of absolute alcohol, was heated on a water-bath for two, three and one-half, or seven hours, respectively, and then poured into 250 cc. of cold water. The monophenoxy derivative, after two recrystallizations from alcohol, was obtained in 40% yield as colorless silky crystals; the diphenoxy, after two recrystallizations from chloroform (in which iodine was liberated slowly) as colorless needles. Attempts to secure the triphenoxy derivative in crystalline form were unavailing, only a yellow, amorphous mass being obtained.

The mono-substituted ester was hydrolyzed incompletely by heating with 30% aqueous potassium hydroxide for several hours. The reaction mixture was poured into water, filtered and the free acid precipitated by dilute hydrochloric acid. Saponification of the di- and tri-substituted esters does not occur under similar conditions.

TABLE I

| Phenoxyacetate | M. p., °C. | Formula | Iodine, % Calcd. | Found |
|---|---|---|---|---|
| Ethyl triiodo- | 128.5 | $C_{10}H_9O_3I_3$ | 68.27 | 67.98 |
| Ethyl ditriiodo- | 160.0 | $C_{10}H_{10}O_4I_6$ | 74.02 | 73.77 |
| Ethyl tri-triiodo- | 208–211[a] | $C_{22}H_{11}O_5I_9$ | 76.23 | 76.06 |
| Potassium triiodo- | 211 (free acid) | $C_8H_4O_3I_3K$ | 67.07 | 66.63 |

[a] Decomposition point.

(1) Hewett, Johnson and Pope, *J. Chem. Soc.*, **103**, 1630 (1913).

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## The Effect of Helium on the Kinetics of the Thermal Decomposition of Acetaldehyde

BY C. J. M. FLETCHER

The extent to which organic molecules decompose by way of a free radical and chain mechanism, or by a simple rearrangement, has been a matter of considerable debate. Although there is an increasing body of experimental evidence which indicates that free radicals and chain processes do exist in the decomposition of such molecules, there is still the alternative that molecular rearrangement can compete with the chain mechanism often to its virtual exclusion. Acetaldehyde is a substance for which a chain mechanism has been proposed,[1] and it has been suggested that the kinetics of its chain decomposition in the presence of free radicals produced either photochemically,[2] or by the thermal decomposition of azomethane,[3] support such a mechanism. However, the concentration of free radicals present,[4] the influence of small amounts of nitric oxide,[5] and the catalysis of acetaldehyde by diethyl ether[6] do not support this hypothesis.

(1) F. O. Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).
(2) Leermakers, *ibid.*, **56**, 1537 (1934).
(3) Allen and Sickman, *ibid.*, **56**, 2031 (1934).
(4) Patet, *Z. physik. Chem.*, **B32**, 294 (1936).
(5) Staveley and Hinshelwood, *J. Chem. Soc.*, 812 (1936).
(6) Fletcher and Rollefson, THIS JOURNAL, **58**, 2129 (1936).

The effect of inert gases on the rate of reaction also indicates that the decomposition does not follow the chain mechanism:

$$CH_3CHO \longrightarrow CH_3 + CHO \quad k_1 \quad E_1 \quad (1)$$
$$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO \quad k_2 \quad E_2 \quad (2)$$
$$CH_3.CO \longrightarrow CH_3 + CO \quad k_3 \quad E_3 \quad (3)$$
$$2CH_3 \longrightarrow C_2H_6 \quad k_4 \quad E_4 \quad (4)$$
$$2CH_3 + M \longrightarrow C_2H_6 + M \quad k_5 \quad E_5 \quad (5)$$

but rather the direct rearrangement

$$CH_3CHO \longrightarrow CH_4 + CO \quad k_6 \quad E_6 \quad (6)$$

for whereas at temperatures above 440°, the recombination of methyl radicals is mainly a homogeneous reaction which takes place partially at ternary collisions so that the rate of the chain reaction is retarded by helium,[7] the thermal decomposition of acetaldehyde itself is accelerated by nitrogen,[8] and by helium (Table I).

TABLE I

TEMPERATURE 552°

| $p_{Acet.}$, mm. | $p_{He}$, mm. | $t_{1/2}$, sec. | $t_{1/2}/t_{1/2}$ | Increase in $1/t_{1/2}$, % |
|---|---|---|---|---|
| 93.9 | 429 | 148 | 1.97 | 11 |
| 82.0 | 375 | 160 | 1.95 | 10 |
| 96.4 | ... | 163 | 1.94 | .. |
| 83.0 | ... | 175 | 1.93 | .. |

The last column of Table I gives the increase in rate (as determined from values of the time taken for the pressure to increase by one-third of the initial pressure of acetaldehyde) in the presence of helium compared to the rate for the same initial pressure of pure acetaldehyde.

The results with helium were obtained with the same experimental procedure as that for which it was found that the rate of the chain decomposition in the presence of ethylene oxide was retarded by about 10% at 441° for a 2:1 helium ratio.[7] As the heterogeneous recombination of methyl radicals decreases with temperature, the acceleration given in Table I cannot be accounted for by the inert gas preventing the diffusion of radicals to the walls. Neither can it be explained on the chain mechanism by an increase in the rate of production of methyl radicals such as might occur if reaction 1 were second order; for the initial rate of the chain mechanism is

$$-(dp/dt) = p^{(n/2)+1} k_2 \sqrt{k_1/[k_4 + k_5 (M)]} \quad (1)$$

where $n$ is the order of reaction 1, so that to explain the observed order of approximately 1.5, Reaction 1 has to be first order.

As the chain mechanism competes so ineffectively with the direct rearrangement, it may be assumed that its over-all energy of activation, $E_{ald.}$, is considerably higher. If the variation with temperature of the recombination of free radicals at ternary collisions can be neglected, then, from equation 1, $E_{ald.} = E_2 + {}^1/_2(E_1 - E_4)$. Values of $(E_2 - {}^1/_2E_4)$ may be obtained from the decompositions induced by azomethane and ethylene oxide; from the results with azomethane, Allen and Sickman[8] derived the value 13,800 cal. on the assumption, which is probably justified,[9] that all the azomethane decomposes to give free radicals. With ethylene oxide the fraction of molecules which gives free radicals is approximately 14%;[7] if the temperature independent factors are the same for both types of decomposition, such a proportion would be obtained if the energies of activation differ by about 3000 cal., *i. e.*, that for the production of free radicals would be approximately 56,000 cal. Making a calculation similar to that for azomethane, $(E_2 - {}^1/_2E_4)$ is therefore 13,500 cal., in good agreement with the value from azomethane. Thus $E_{ald.} \simeq {}^1/_2E_1 + 13{,}700$ cal., so that for the chain mechanism to have a larger energy of activation than that actually observed (50,000 cal.[10] or 45,700 cal.[11]), the energy of activation ($E_1$) for the breaking of the C–C bond must be closer to 80,000 cal. than to the value of 70,000 cal. assumed by Rice and Herzfeld.

(7) Fletcher and Rollefson, THIS JOURNAL, **58**, 2135 (1936).

(8) Hinshelwood and Askey, *Proc. Roy. Soc.* (London), **A128**, 91 (1930).

(9) O. K. Rice and Sickman, *J. Chem. Phys.*, **4**, 242 (1936).

(10) Fletcher and Hinshelwood, *Proc. Roy. Soc.* (London), **A141**, 41 (1933).

(11) Letort, *Compt. rend.*, **199**, 1617 (1934).

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BERKELEY, CALIF. RECEIVED SEPTEMBER 15, 1936

## The Standard Electrode Potential of Silver

BY J. J. LINGANE AND W. D. LARSON

The value for the standard potential of the silver electrode, $Ag \mid Ag^+$ ($a = 1$), given by Lewis and Randall[1] is −0.7995 v., whereas the value given in the "International Critical Tables"[2] is −0.7978 v. Both of these values apparently are based on the measurements of Noyes and Brann[3] on cells involving liquid junction potentials. Evaluation of the standard potential of the silver electrode from these measurements

(1) Lewis and Randall, "Thermodynamics," McGraw Hill Book Co., Inc., New York, 1923, p. 414.

(2) "International Critical Tables," Vol. VI, p. 333.

(3) Noyes and Brann, THIS JOURNAL, **34**, 1016 (1912).