

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 pro-

nounced 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.

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## NOTES

### The Ethyl Esters of Triiodophenoxyacetic Acids and Potassium Triiodophenoxyacetate

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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<sup>1</sup> 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 potas-

sium 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.

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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,<sup>1</sup> and it has been suggested that the kinetics of its chain decomposition in the presence of free radicals produced either photochemically,<sup>2</sup> or by the thermal decomposition of azomethane,<sup>3</sup> support such a mechanism. However, the concentration of free radicals present,<sup>4</sup> the influence of small amounts of nitric oxide,<sup>5</sup> and the catalysis of acetaldehyde by diethyl ether<sup>6</sup> 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).

TABLE I

Phenoxyacetate	M. p., °C.	Formula	Iodine, %	
			Calcd.	Found
Ethyl triiodo-	128.5	C <sub>10</sub> H <sub>9</sub> O <sub>3</sub> I <sub>3</sub>	68.27	67.98
Ethyl di- iodo-	160.0	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub> I <sub>2</sub>	74.02	73.77
Ethyl tri- iodo-	208-211 <sup>a</sup>	C <sub>22</sub> H <sub>11</sub> O <sub>5</sub> I <sub>3</sub>	76.23	76.06
Potassium triiodo-	211 (free acid)	C <sub>3</sub> H <sub>4</sub> O <sub>3</sub> I <sub>3</sub> K	67.07	66.63

<sup>a</sup> Decomposition point.

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