iodide ions, reaction D has been investigated with different concentrations of free iodine and constant concentrations of potassium iodide and iodoacetic acid. In D1 the quantity of free iodine was equivalent to $^1/_3$ of the quantity of iodide present, in D2 this ratio was $^1/_2$ and in D3 it was $^2/_3$. The concentration of sulfuric acid has been 0.005 molar in all experiments.

TABLE II

OBSERVED AND CALCULATED REACTION CONSTANTS FOR EXCHANGE AGAINST RADIOACTIVE MONOIODIDE AND TRIIODIDE

	Reaction A	Reaction D1	Reaction D2	Reaction D3
Concn. KI (moles l. $^{-1}$)		0.0046	0.0046	0.0046
Concn. I_2 (moles l. $^{-1}$)	0	.00147	.0023	.0030
Concn. CH_2ICOOH (moles l. $^{-1}$)		.0093	.0093	.0093
Exp. react. const. (moles l. $^{-1}$ sec. $^{-1}$)	0.0087	.0049	.0041	.0031
$\frac{\text{Calc. concn. I}^-}{\text{total concn. I}^-} \times 0.0087$ (moles l. $^{-1}$ sec. $^{-1}$) (calcd. with equil. const. = 0.0014)	.0087	.0067	.0057	.0049
$\frac{\text{Calc. concn. I}^-}{\text{total concn. I}^-} \times 0.0087$ (moles l. $^{-1}$ sec. $^{-1}$) (calcd. assuming no free I_2 in sol.)	.0087	.0059	.0043	.0030

The results are given in Table II. Apart from the concentrations used and the experimental values of the reaction constant k, the values of the reaction constant found in the monoiodide experiments multiplied with the ratio of the real monoiodide concentration and the concentration of added potassium iodide are given too. This real monoiodide concentration has been calculated with the aid of the equilibrium: $I^- + I_2 \rightleftarrows I_3^-$, using an equilibrium constant of about 0.0014[6] and also assuming that no free iodine remains in the solution. The formation of higher polyiodides has been neglected. If the exchange of radioactive iodine between the organic molecules and the I_3^- ions is very slow compared with the exchange with normal iodide ions, we can calculate the experimental velocity constant in the following manner[7]

a = concn. $CH_2ICOOH + CH_2I^*COOH$
b = total concn. $I^- + I^{*-} + I_3^- + I_3^{*-}$
c = real concn. $I^- + I^{*-}$
x = concn. CH_2I^*COOH at time t
y = total concn. $I + I_3^{*-}$ at time t
z = real concn. I^{*-} at time t
k_e = exptl. bimolecular reaction constant calcd. with the assumption that I^- and I_3^- react with equal ease
k_t = theoretical bimolecular reaction constant calcd. with the assumption that I_3^- reacts much slower than I^-

The formation velocity of active iodoacetic acid is

$$dx/dt = k_e[y(a - x) - x(b - y)] = k_e(ya - xb) \quad (1)$$

or

$$dx/dt = k_t[z(a - x) - x(c - z)] = k_t(za - xc) \quad (2)$$

The exchange between the free iodine and the iodine ions is very fast,[8] so

$$z/c = y/b \quad (3)$$

$$dx/dt = k\frac{c}{tb}(ya - xb) \quad (4)$$

$$k_e = c/bk_t \quad (5)$$

From Table II it is seen that the exchange reaction between I_3^- and CH_2ICOOH is much slower than the reaction between I^- and CH_2ICOOH; no conclusions can be drawn regarding the velocity of the former process.

Acknowledgment.—This investigation represents part of the research program of the Foundation for Fundamental Research of Matter (F.O.M.). It was performed with the financial aid of the Netherlands Organization for Pure Research (Z.W.O.).

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(6) J. S. Carter, *J. Chem. Soc.*, 2227 (1928).

(7) R. D. Heyding and C. A. Winkler, *Can. J. Chem.*, **29**, 790 (1951).

(8) D. E. Hull, C. H. Shiflet and S. C. Lind, THIS JOURNAL, **58**, 535 (1936).

AMSTERDAM, HOLLAND

[CONTRIBUTION NO. 323 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE[1]]

The Kinetics of the Reduction of Perchlorate Ion by Ti(III) in Dilute Solution

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RECEIVED FEBRUARY 6, 1954

The reduction of perchlorate ion by Ti(III) in dilute solutions appears to proceed by several paths. The reaction has $[H^+]$ dependent as well as $[H^+]$ independent paths. The addition of chloride retards the reaction, apparently due to the formation of $TiCl^{+2}$ ion. The reaction is linear in ClO_4^- at concentrations below about 1.0 *M*. Above this concentration the reaction rate increases, this probably being due to the increased activity coefficient of the perchlorate ion at higher concentrations. There was insufficient complex ion formation between Ti(III) and ClO_4^- to be kinetically detectable. The activation energies for the various reactions were calculated and a mechanism proposed.

Introduction

The reduction of perchlorate ion by Ti(III) at room temperatures and slightly above proceeds to completion at a convenient rate with the production of Cl^- and Ti(IV)

$$8Ti(III) + ClO_4^- + 8H^+ \longrightarrow 8Ti(IV) + Cl^- + 4H_2O$$

Preliminary work on the reduction of perchlorate ion by Ti(III) in dilute solutions was done by Bredig and Michel.[2] They studied the kinetics of the oxidation of trivalent titanium compounds with perchloric acid in aqueous sulfuric acid and hydrochloric acid solutions, as well as the rate of reaction of $HClO_4$ with Cr(II) and Mo(II) compounds.

This present work examines more in detail the Ti(III)–ClO_4^- reaction in solutions containing chlo-

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(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) G. Bredig and J. Michel, *Z. physik. Chem.*, **100**, 124 (1922).

ride. A kinetic mechanism to explain the observed data has been presented.

Experimental

All chemicals used were reagent grade. The $TiCl_3$ solutions were prepared by dissolving titanium metal powder from Metal Hydrides, Inc., Beverly, Massachusetts, in approximately 6 *N* HCl. All solutions of $TiCl_3$ were prepared and stored under an atmosphere of nitrogen. Total chloride was determined by the nitrobenzene modification of the Volhard method for soluble chlorides. The Ti(III) was first oxidized with excess Ce(IV) to prevent reduction of the Ag^+. The Ti(III) was standardized by "A.O.A.C." Method I.[3] The H^+ was taken to be the difference between the Ti(III) and total chloride concentration. $NaClO_4$ was prepared by neutralizing 70–72% $HClO_4$ with NaOH pellets. This was then standardized by passing through an acid exchange resin and titrating the acid produced with standard base. NaCl solutions were made by dissolving the required amount of the salt in water. HCl and $HClO_4$ solutions were used and standardized with standard NaOH.

TABLE I

Experiments run: *All*, starting Ti(III) concentration, 0.15 *M;* Ti(III) determined as a function of time; all concentrations in molarity.

$[H^+]$	$[Cl^-]$	$[ClO_4^-]$	*T*, °C.
0.23–1.0 (5 values)	2.0	0.50	30, 40, 50
0.22	0.24–1.4 (7 values)	0.50	40, 50
0.50	0.24–1.4 (7 values)	0.50	40, 50
0.75	0.26–1.6 (8 values)	0.50	40, 50
1.0	0.51–1.4 (6 values)	0.50	40, 50
0.22	2.0	0.02–2.0 (15 values)	40
0.5	2.0	0.1–2.0 (15 values)	40
1.0	2.0	0.1–2.0 (15 values)	40
0.23	0.24	0.25–6.0 (13 values)	20

Each run was made in the following manner: The NaCl, $NaClO_4$, $HClO_4$ and HCl necessary to make up a solution of the desired concentration were added to a 100-ml. volumetric flask with an extra calibration mark at 96 ml. The solution was diluted to the 96-ml. mark and placed in a water-bath for about one half hour to allow it to come to the desired temperature. The determinations were made in a distilled water-bath using a mercury thermoregulator to control the temperature to ±0.05°. Four ml. of the $TiCl_3$ solution was added, the solution shaken thoroughly, and the timer started. At known intervals of time 5-ml. samples were removed and quenched in an excess of quenching solution. This consisted of a solution of 0.01 *N* ceric ammonium sulfate approximately 9 *N* in H_2SO_4. The time of quenching was taken as the time at which the meniscus passed a mark on the pipet, usually the halfway mark. The excess Ce(IV) was then titrated with ferrous ammonium sulfate using ferroin as indicator. First-order plots were made from ln $[T_{Ti^{+3}}]$ *vs.* time. The experiments run are summarized in Table I.

Results and Discussion

Straight lines were obtained when $\ln[T_{Ti^{+3}}]$ was plotted against time. This confirmed the results of Bredig and Michel, who also found the reaction between Ti(III) and ClO_4^- first order in Ti(III). The rate expression for the disappearance of Ti(III) may be written

$$-\frac{d[T_{Ti^{+3}}]}{dt} = k[T_{Ti^{+3}}]F_1([ClO_4^-]),([Cl^-]),([H^+]) \quad (1)$$

Here *k* represents the specific rate constant for the reaction and F_1 is some function of the ion concentrations as yet to be determined. For any one run, the ClO_4^- concentration is large compared to the Ti(III), and the H^+ and Cl^- are constant so that this expression becomes

$$-\frac{d[T_{Ti^{+3}}]}{dt} = k'[T_{Ti^{+3}}] \quad (2)$$

where k' is the pseudo first-order rate constant. k' is the slope of a plot of $\ln[T_{Ti^{+3}}]$ *vs.* time. By keeping all concentrations of the ions constant except the one whose dependence is being determined it was possible to determine the effects of H^+, Cl^- and ClO_4^-, on the rate of reaction. The ionic strength was allowed to vary, since two concentrations would have to have been varied simultaneously to keep the ionic strength constant.

The reaction was found to be linear in ClO_4^- at concentrations less than about 1.0 *M*. Above this concentration the rate increases as shown in Fig. 1

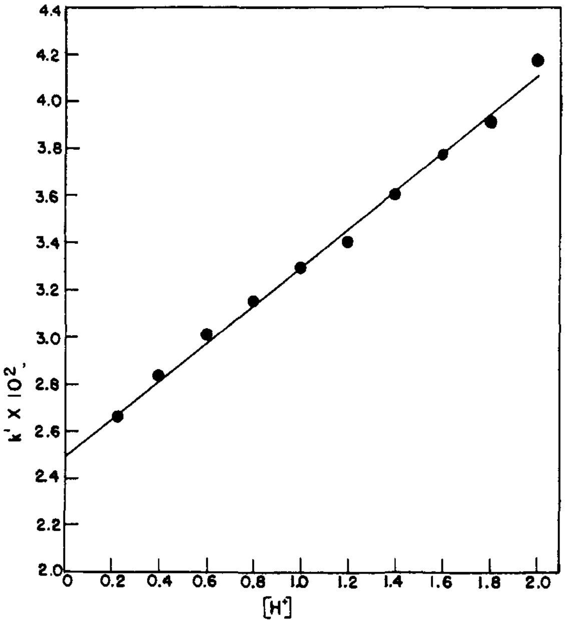

Fig. 1.—Hydrogen ion dependence 40°; first-order rate constants *versus* $[H^+][Ti^{+3}] = 0.015$ *M*, $[ClO_4^-] = 0.5$ *M*, $[Cl^-] = 2.0$ *M*.

The possibility of the formation of any Ti(III)–ClO_4^- complexes was investigated. Runs were made at ClO_4^- concentrations up to 6 *M* and no lowering of the order in ClO_4^- was observed. The increased rate at higher ClO_4^- concentration is probably due to the increased activity of ClO_4^- and the correspondingly decreased activity of the water. This behavior was shown by Robinson and Baker.[4]

The hydrogen ion dependence was determined at $Cl^- = 2$ *M*, $ClO_4^- = 0.05$ *M*, and original Ti(III) $= 0.015$ *M*, and at 40°. The data are shown

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[3] Association of Official Agricultural Chemists, "Methods of Analysis," 6th Ed., 1945, p. 290.

[4] R. A. Robinson and O. J. Baker, *Trans. Proc. Roy. Soc. New Zealand*, **76**, 250 (1946).

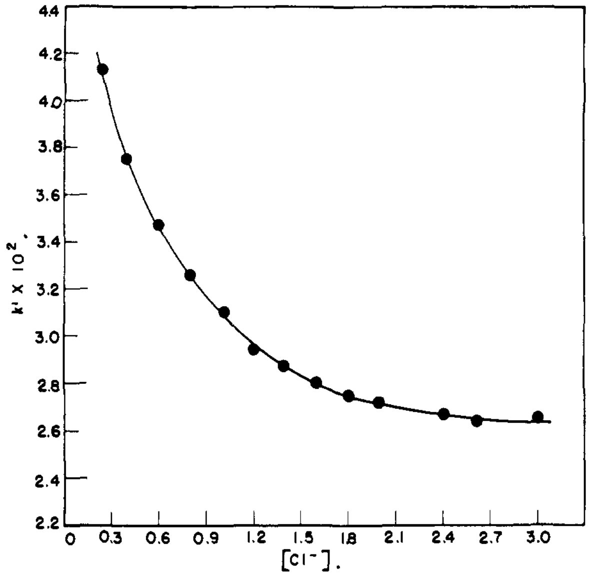

Fig. 2.—Chloride ion dependence 40°; first-order rate constants *versus* $[Cl^-]$ $[Ti^{+3}] = 0.015\ M$, $[ClO_4^-] = 0.5\ M$, $[H^+] = 0.5\ M$.

plotted in Fig. 2. When k' is plotted against H^+ a straight line is obtained which does not pass through the origin. So the H^+ dependence is of the form

$$k' = k_{0H} + k_{1H}\,[H^+] \qquad (3)$$

where k_{0H} and k_{1H} are the rate constants for the hydrogen ion independent and the H^+ catalyzed reactions, respectively.

The effect of chloride ion was studied at $ClO_4^- = 0.5\ M$, $H^+ = 0.5\ M$, Ti(III) $= 0.015\ M$, and the same temperature. Chloride ion tends to retard the reaction considerably at concentrations less than 2 M. A typical graph for the behavior of the Cl^- dependence is shown in Fig. 3. If one assumes complex ion formation between Ti(III) and Cl^-, it is to be expected that the rate of reaction will depend upon the titanium species reacting with the perchlorate. It appears, for example, that titanium complexes with chloride react more slowly than uncomplexed titanium.

If one considers the rate of this reaction at Cl^- less than 2 M, and ClO_4^- less than about 1.0 M, the rate expression may be written

$$-\frac{d[T_{Ti^{+3}}]}{dt} = k_1[Ti^{+3}][ClO_4^-] + k_2[TiCl^{++}][ClO_4^-] + k_3[Ti^{+3}][ClO_4^-][H^+] + k_1[TiCl^{+2}][ClO_4^-][H^+] \qquad (4)$$

Now total titanium is

$$T_{Ti^{+3}} = Ti^{+3} + TiCl^{++} \qquad (5)$$

and

$$K_1 = \frac{[TiCl^{++}]}{[Ti^{+3}][Cl^-]} \qquad (6)$$

Writing the rate expression, equation 4, in terms of total titanium

$$-\frac{d[T_{Ti^{+3}}]}{dt} = \frac{k_1 + k_2K_1[Cl^-] + k_3[H^+] + k_4K_1[Cl^-][H^+]}{1 + K_1[Cl^-]}\,[ClO_4^-][T_{Ti^{+3}}] \qquad (7)$$

This is the rate expression found from experiment.

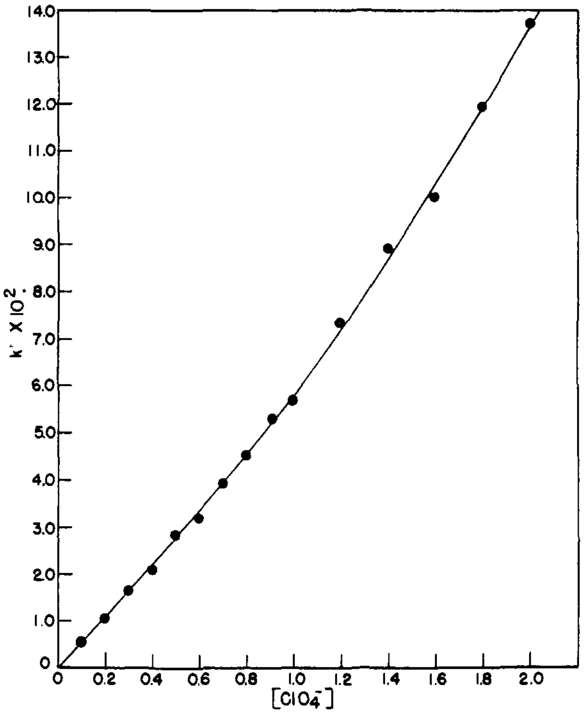

Fig. 3.—Perchlorate ion dependence 40°; first-order rate constants *versus* $[ClO_4^-]$ $[Ti^{+3}] = 0.015\ M$, $[Cl^-] = 2.0\ M$, $[H^+] = 0.5\ M$.

The equilibrium constant K_1 was determined from a study of the chloride dependence. The rate constants were separated and determined by considering the rate expression first at constant H^+ and then at constant Cl^-.

At constant H^+, the rate equation becomes

$$-\frac{d[T_{Ti^{+3}}]}{dt} = \frac{k_1' + k_2'K_1[Cl^-]}{1 + K_1[Cl^-]}\,[ClO_4^-][T_{Ti^{+3}}] \qquad (8)$$

where

$$k_1' = k_1 + k_3[H^+]$$

and

$$k_2' = k_2 + k_4[H^+]$$

The pseudo first-order rate constant may then be written

$$\frac{k'}{[ClO_4^-]} = \frac{k_1' + k_2'K_1[Cl^-]}{1 + K_1[Cl^-]} \qquad (9)$$

The constants k_1' and k_2' were determined at various H^+, the Cl^- and ClO_4^- concentrations being the same and constant for each determination. Plots of k_1' and k_2' *vs.* H^+ yielded straight lines, the slopes of which were k_3 and k_4, and the intercepts of which were k_1 and k_2, respectively.

Considering the rate expression at constant chloride, the pseudo constant becomes

$$\frac{k'(1 + K_1')}{[ClO_4^-]} = k_1'' + k_2''[H^+] \qquad (10)$$

where

$$K_1' = K_1[Cl^-]$$
$$k_1'' = k_1 + k_2K_1[Cl^-]$$

and

$$k_2'' = k_3 + k_4K_1[Cl^-]$$

A plot of k' *vs.* H^+ was made for different values of Cl^-. This yielded a series of straight lines which have slopes of k_2'' as a function of Cl^-, and intercepts with values of k_1'' at various Cl^-. A plot is then made of k_1'' *vs.* Cl^- and k_2'' *vs.* Cl^-. These plots yield straight lines which have slopes of k_1 and k_2 and intercepts of k_2K_1 and k_4K_1, respectively. The rate constants were calculated and the average values are shown in Table II.

TABLE II

RATE AND EQUILIBRIUM CONSTANTS 40°

$[Ti^{+3}] = 0.015\ M$, $[ClO_4^-] = 0.5\ M$

$k_1 \times 10^2$	$k_2 \times 10^2$	$k_3 \times 10^3$	$k_4 \times 10^2$	K_1
8.89 ± 0.9	3.59 ± 0.4	3.40 ± 0.3	1.36 ± 0.2	2.18 ± 0.2

The rate constants were determined at both 40 and 50°. The energies of activation and the entropies of activation for the various steps in the reaction were then calculated. The results are shown in Table III.

TABLE III

ACTIVITY ENERGIES AND ENTROPIES 40°

$k_1 \times 10^2$	8.89 ± 0.9	$k_4 \times 10^2$	1.36 ± 0.2
$\Delta F^‡_{313}$, kcal.	19.9 ± 0.1	$\Delta F^‡_{313}$, kcal.	21.0 ± 0.1
$\Delta H^‡$, kcal.	26 ± 15%	$\Delta H^‡$, kcal.	10 ± 50%
$\Delta S^‡$, e.u.	20 ± 50%	$\Delta S^‡$, e.u.	−36 ± 50%
$k_2 \times 10^2$	3.5 ± 0.4	K_1	2.18 ± 0.2
$\Delta F^‡_{313}$, kcal.	20.4 ± 0.1	ΔF_{313}, kcal.	17.8 ± 0.1
$\Delta H^‡$, kcal.	25 ± 14%	ΔH, cal.	2500 ± 50%
$\Delta S^‡$, e.u.	17 ± 50%	ΔS, e.u.	−50 ± 100%
$k_3 \times 10^3$	3.40 ± 0.3		
$\Delta F^‡_{313}$, kcal.	20.4 ± 0.1		
$\Delta H^‡$, kcal.	6 ± 50%		
$\Delta S^‡$, e.u.	−46 ± 50%		

The reaction is thought to proceed through the formation of an activated complex, the disproportionation of which is the rate-determining step. The following four equations have been proposed to explain the kinetics of the reaction

$$Ti^{+3} + ClO_4^- \rightleftarrows [\text{complex}] \longrightarrow TiO^{++} + ClO_3$$

$$Ti^{+3} + ClO_4^- + H^+ \rightleftarrows [\text{complex}] \longrightarrow Ti(OH)^{+3} + ClO_3$$

$$TiCl^{++} + ClO_4^- \rightleftarrows [\text{complex}] \longrightarrow TiO^{++} + ClO_3 + Cl^- \ [\text{or } TiOCl^+]$$

$$TiCl^{++} + ClO_4^- + H^+ \rightleftarrows [\text{complex}] \longrightarrow Ti(OH)^{+3} + ClO_3 + Cl^- \ [\text{or } TiOHCl^{+2}]$$

From the standpoint of the free energies involved and the probability of reaction most likely to occur, the first and third equations above would seem to be the most important. The radical ClO_3 is rapidly reduced further to the final product Cl^-. It may well be true that the affinity of the Ti(IV) for OH^- and $O^=$ accounts for the low activation energy of this reaction as compared with reductions of perchlorate with Fe(II), Sn(II), Cr(II) and others.

AMES, IOWA

[CONTRIBUTION NO. 321 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE[1]]

The Kinetics of the Periodate Oxidation of Ethylene Glycol and a Series of Methylated Ethylene Glycols

BY FREDERICK R. DUKE AND VERNON C. BULGRIN

RECEIVED FEBRUARY 8, 1954

The specific periodate oxidation of the homologous series of glycols, ethylene glycol through pinacol, shows a discontinuity in mechanism between trimethylethylene glycol and pinacol. The latter is very slowly oxidized in an acid-catalyzed bimolecular step, while the former, as with the other glycols studied, proceeds rapidly in a non-catalyzed unimolecular step. The effect of stepwise methyl group substitution in ethylene glycol is determined, both in the free energy of complex formation with periodate and on the unimolecular rate constant.

The mechanism of the periodic acid cleavage of ethylene glycol may involve an intermediate coördination compound of the oxidant and reductant, the rate-determining step being the disproportionation of the intermediate.[2] The rate of the reaction has been demonstrated to be nearly independent of hydrogen ion concentration in the *p*H range three to seven.[2,3] Waters[4] attributed the constancy of the rate in this region to the fact that hydrogen ion catalysis is balanced by decreasing ionization of H_5IO_6 to the reactive $H_4IO_6^-$. Crouthamel, Martin and co-workers, in a spectrophotometric study of periodate species in solution,[5,6] showed that the concentration of negative ion, predominantly IO_4^-, is nearly constant in the *p*H range three to seven.

Price[3] found the rate of oxidation of pinacol to be a peculiar function of hydrogen ion concentration, having a sharp maximum at *p*H 2 and a minimum for the range four to six.

A kinetic study of the oxidation of the series ethylene glycol through pinacol was undertaken, in an effort to observe the effect of methyl substitution on the rate and equilibrium constants and to determine at which point in the series the change in reactivity exhibited by pinacol begins to show up.

Experimental

Ethylene and propylene glycols obtained from the Matheson Co. were twice distilled before using. *meso*-2,3-Butanediol, which had been prepared by the fermentation of corn using *Aerobacter aerogenes*,[7] was purified by recrystallization from dry isopropyl ether.[8] *levo*-2,3-Butanediol was pre-

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] F. R. Duke, THIS JOURNAL, **69**, 3054 (1947).

[3] C. C. Price and M. Knell, *ibid.*, **64**, 552 (1942).

[4] W. A. Waters in H. Gilman, "Organic Chemistry," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1953, Chap. 12.

[5] C. Crouthamel, H. V. Meek, D. S. Martin and C. V. Banks, THIS JOURNAL, **71**, 3031 (1949).

[6] C. Crouthamel, A. Hayes and D. S. Martin, *ibid.*, **73**, 82 (1951).

[7] E. R. Kooi, E. I. Fulmer and L. A. Underkofler, *Ind. Eng. Chem.*, **40**, 1440 (1948).

[8] C. E. Wilson and H. J. Lucas, THIS JOURNAL, **58**, 2396 (1936).