use in the Stobbe condensation. The preliminary results of our study were so promising that we are announcing them herewith. The new procedure appears to afford some advantage over the *t*-butoxide method in that it is considerably simplified, while the yields with two representative ketones, acetophenone and benzophenone, are at least as good. In a future communication we expect to report on a more extensive study of this new modification as well as on the mechanism of the condensation.

Experimental[3]

Stobbe Condensation with Acetophenone.—A mixture of 6.00 g. (0.05 mole) of the ketone, 26.13 g. (0.15 mole) of diethyl succinate and 2.4 g. (0.1 mole) of sodium hydride[4] was stirred for three and three-quarters hours at room temperature, care being taken to exclude all moisture from reagents and apparatus. The rate of evolution of hydrogen which was very slow at first graduallyincreased until after two hours it became quite rapid, slackening off toward the end of the reaction period. After three hours, 10 ml. of anhydrous benzene was added to facilitate stirring. The mixture was acidified with acetic acid, and extracted with ether. The ether solution was extracted with 5% sodium bicarbonate solution which on acidification gave 11.59 g. (93.5% yield) of pale yellow semi-solid acid undoubtedly consisting of a mixture of isomeric half-esters of Stobbe condensation product (neut. equiv., calcd., 248; found, 261). Crystallization from petroleum ether (b. p. 60–68°) rendered about one-third of the material crystalline; m. p. 111–112° after recrystallization from benzene–petrolum ether. This is probably identical with the half-ester of γ-methyl-γ-phenylisoitaconic acid, described by Stobbe[5] as melting at 110–112°. Saponification of the 112° half-ester with barium hydroxide afforded the crystalline dibasic acid, m. p. 180–182° with dec. (reported,[5] 178–179° and 183–185° with dec.).

Extraction of the ether solution, remaining after removal of the bicarbonate-soluble fraction, with 5% potassium hydroxide solution gave 1.23 g. of crude diethyl 1,4-diketocyclohexane-2,5-dicarboxylate, m. p. 117–123.5°, arising from the self-condensation of diethyl succinate. Recrystallization from alcohol raised the melting point to 126–127.5°, undepressed on admixture with an authentic specimen. This product gave a deep cherry-red color with alcoholic ferric chloride solution.

With Benzophenone.—When 9.11 g. (0.05 mole) of benzophenone and 26.13 g. (0.15 mole) of diethyl succinate were treated with 2.4 g. (0.1 mole) of sodium hydride as described above, no appreciable reaction took place even at steam-bath temperature. The addition of 10 drops of ethanol, however, initiated the reaction which proceeded readily at room temperature. The rate of hydrogen evolution increased as the reaction progressed until the sodium hydride was consumed (about eight hours). After about five hours 25 ml. of dry ether was added to facilitate the stirring of the mixture, which had become quite thick. The bicarbonate-soluble material, isolated as described above, amounted to 15.05 g. (a 97% yield) of almost colorless crystals, m. p. 124.5–125.5°, undepressed on admixture with an authentic specimen of β-carbethoxy-γ,γ-diphenylvinylacetic acid (m. p. 125–126°).[1c]

The 1,4-diketocyclohexane-2,5-dicarboxylate isolated by extraction with potassium hydroxide amounted to 1.58 g., m. p. 119–123.5°.

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[3] All melting points are corrected.

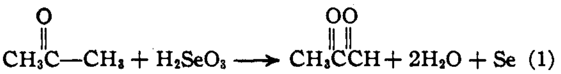
[4] Procured from Electrochemicals Department, E. I. du Pont de Nemours and Company.

[5] Stobbe, *Ann.*, **308**, 114 (1899).

Kinetics of the Oxidation of Acetone by Selenious Acid

BY FREDERICK R. DUKE

The discovery of intermediates in appreciable concentration during the glycol-splitting type of specific oxidation[1] prompted this investigation of the selenious acid–acetone reaction. The stoichiometry is represented by the equation[2]



$$CH_3\overset{\overset{O}{\|}}{C}—CH_3 + H_2SeO_3 \longrightarrow CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}H + 2H_2O + Se \quad (1)$$

The reaction was studied extensively by Mel'nikov and Rokitskaya.[3] They found that the common alkyl esters of selenious acid decomposed at high temperatures to yield the corresponding aldehyde or ketone and selenium, and from this concluded that the oxidation of aldehydes and ketones proceeded through the enol ester intermediate. Data on the ease of oxidation of a series of aldehydes and ketones was used by these investigators to arrange the compounds in order of ease of enolization.

In the present investigation, the effects of high hydrogen ion and acetone concentrations on the rate of the reaction were studied in an attempt to demonstrate kinetically the presence of an intermediate. The data obtained clearly show that no appreciable amount of intermediate accumulates; however, certain conclusions may be drawn from the results and these are presented below.

Experimental

C. P. reagents were used. The specific gravity of the acetone was 0.7890 (25°/4°), fixing the water content at less than 1.5%.[4] Fifty-ml. volumetric flasks were used as reaction vessels; in Experiments I the appropriate amount of 5 *M* perchloric acid, 5 *M* sodium perchlorate, pure water and acetone and 2.0 ml. of 0.1 *M* selenious acid were pipetted into the flasks; then the latter were filled to the mark with *t*-butanol. After fifteen minutes in the constant temperature bath, sampling was begun with a 5-ml. pipet. The samples were quenched in acidified 5% KI solution, and the iodine titrated with 0.01 *N* thiosulfate. *t*-Butanol was used to maintain the reaction mixture at approximately constant dielectric as the acetone concentration was varied; the alcohol possesses the additional desirable property of low reactivity in esterification and aldol formation.

Experiments II were run in the same manner as Experiments I, except that the reacting mixture was prepared from 2 *M* acetone and 2 *M* perchloric acid. The acetone concentration was kept sufficiently low that the solutions in all cases may be considered truly aqueous. Sodium perchlorate was added where necessary to maintain constant ionic strength.

Experiments III were identical with the low-temperature runs of Experiment I except that the water concentration was varied and the acetone kept constant.

The constant temperature-bath was water maintained to ±0.1°.

Results.—In each of the experiments, the concentrations of reactants were chosen such that

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[1] Duke, THIS JOURNAL, **69**, 2885 (1947); **69**, 3054 (1947).

[2] Riley, Morley and Friend, *J. Chem. Soc.*, 1875–1883 (1932).

[3] Mel'nikov and Rokitskaya, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 1532–1538, 2738–2746 (1937); **8**, 1369–1380 (1938); **9**, 1158–1161, 1808–1812 (1939); **10**, 1439–1441, 1713–1716 (1940).

[4] Hughes and Hartley, *Phil. Mag.*, [7] **15**, 61 (1933).

essentially only the selenious acid concentration changed. Plots of log $[H_2SeO_3]$ *vs.* time yielded straight lines, the slopes being the first order (in oxidant) pseudoconstants.

The results of Experiments I are listed in Table I. It is evident that the reaction is first-order in acetone over a wide range of concentration. Experiments II (Table II) run at relatively low acetone concentrations and in aqueous solution to ensure incontrovertible meaning for $[H^+]$, demonstrate that equation I holds over a wide range of acidity

$$-d[H_2SeO_3]/dt = k\,[\text{acetone}][H_2SeO_3][H^+] \quad (I)$$

No acidities lower than 0.04 *N* were studied because at higher *p*H values the loss of selenious acid from solution would invalidate the assumption that $[H^+]$ remains constant throughout a given run.

TABLE I

PSEUDO-CONSTANTS (1/MIN.) IN WATER–*t*-BUTANOL MIXTURES

$[H_2O] = 22.2$, $[H^+] = 0.50$, concentrations in m./l.

	T 43.1°		*T* 24.0°	
[acetone]	$k' \times 10^3$	$k' \times 10^3$/[acetone]	$k' \times 10^3$	$k' \times 10^3$/[acetone]
1.34	1.64	1.22	0.192	0.143
2.01	2.56	1.27	.290	.144
2.68	3.333	1.24	...	...
3.35	..	..	.488	.146
4.69	5.55	1.18	.680	.145
6.70	7.41	1.11	1.03	.154

TABLE II

PSEUDO-CONSTANTS (1/MIN.) IN AQUEOUS SOLUTION

Concentrations in m./l., *T* 47.1°

$[H^+] = 0.10$			[Acetone] = 0.30		
[acetone]	$k' \times 10^5$	$k' \times 10^5$/[acetone]	$[H^+]$	$k' \times 10^5$	$k' \times 10^5$/$[H^+]$
0.04	0.83	20.8	0.04	2.40	60
.10	2.08	20.8	.10	7.04	70
.20	4.00	20.0	.20	13.0	65
.30	7.04	23.5	.30	20.0	67
.50	12.5	25.0	.50	31.3	63

TABLE III

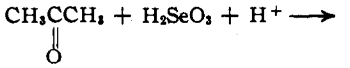
PSEUDO-CONSTANTS (1/MIN.) IN WATER–*t*-BUTANOL MIXTURES

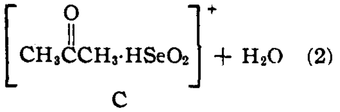
$[H^+] = 0.50$, [acetone] = 4.69, *T* 24.0, concentrations in m./l.

$[H_2O]$	$k' \times 10^3$	$k' \times 10^3 \times [H_2O]$
11.1	0.80	8.9
16.6	.74	11.9
22.2	.68	15.1
33.3	.63	21.0

Experiments III indicate that an increase in the concentration of water results in a lowered reaction rate. These results are discussed below.

Discussion.—Since the stoichiometry of reaction (1), contrary to the kinetics data, requires no hydrogen ion, the logical conclusion is that an intermediate, C, is formed





$$CH_3\underset{\underset{O}{\|}}{C}CH_3 + H_2SeO_3 + H^+ \longrightarrow \underset{C}{\left[CH_3\overset{\overset{O}{\|}}{C}CH_3{\cdot}HSeO_2\right]^+} + H_2O \quad (2)$$

(C, as written, is not intended to include an implication of structure.) Reaction (2) presents two alternative possibilities: that the rate of formation of C is the measurable reaction, equation I correctly designating the kinetics; or that reaction (2) is an equilibrium reaction with $K = [C][H_2O]/[\text{acetone}][H_2SeO_3][H^+]$. In the latter case, the correct kinetics expression is $-d[H_2SeO_3]/dt = kK[\text{acetone}][H_2SeO_3][H^+]/[H_2O]$, since the data demonstrate that no detectable concentration of C is present. The variation in rate with water concentration (Table III) is in the right direction for this equation but is as reasonably explained by changes in activities of reactants with change of solvent. Thus, although no definite conclusion may be reached concerning these possibilities, it seems likely that equation I correctly expresses the kinetics. On this basis, the activation energy for reaction (2) may be calculated to be 18 kcal. per mole.

The Nature of the Intermediate.—One possible structure for C, postulated by Mel'nikov and Rokitskaya[2] is the enol ester. However, Olivier and Berge[5] have shown that for acids similar to selenious, the rate of esterification is not proportional to $[H^+]$. In addition, the oxidation proceeds at a negligible rate in alkaline solution (experiment not reported) under conditions favoring both enolization and esterification. Further, Michaelis and Landmann[6] have demonstrated that diethyl selenite is easily decomposed by pure water, a characteristic of esters whose rates of formation and hydrolysis are relatively independent of acidity.

Consideration of a second structure is dictated by the reaction under similar conditions of sulfurous acid, the closest analog of selenious acid. The preponderance of evidence[7] indicates that acetone and sulfurous acid react to yield an α-hydroxysulfonic acid, the analog being an α-hydroxyselenonic acid. Since, however, no compounds of the type $RSeO_3H$ have ever been prepared directly from selenious acid in spite of repeated attempts to do so,[8] and since the reaction rate of sulfurous acid with carbonyl compounds is inverse to $[H^+]$,[9] it does not seem that the selenonic acid structure deserves further consideration.

The demonstrated basicity of acetone toward selenium dioxide[10] is the basis for a third possibil-

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(5) Olivier and Berge, *Rec. trav. chim.*, **41**, 637 (1922); **46**, 861 (1927).

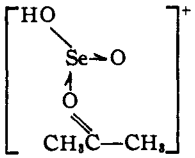
(6) Michaelis and Landmann, *Ann.*, **241**, 150 (1887).

(7) Raschig and Prahl, *Ber.*, **61B**, 179–189 (1928); Stelling, *Cellulosechemie*, **9**, 100–102 (1928); Lauer and Langkammerer, THIS JOURNAL, **57**, 2360–2362 (1935).

(8) Strecker and Daniel, *Ann.*, **462**, 186 (1928).

(9) Stewart and Donnally, THIS JOURNAL, **54**, 3555 (1932).

(10) F. Feigl and E. Feigl, *Z. anorg. allgem. Chem.*, **203**, 60 (1932).

ity =  where the acetone has displaced a hydroxyl ion from the selenium. In favor of this structure, one may cite the complete agreement with the kinetic evidence; but also, the subsequent disproportionation of the intermediate to pyruvaldehyde and selenium is most reasonable. The coördination of the acetone through its oxygen necessarily results in a redistribution of charge within the acetone molecule which would result in enhanced reactivity of the α-hydrogens; and it is not unlikely that the bond distances and angles in the complex are such that the selenium oxygens are placed in a favorable steric position for reaction with α-carbon.

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Iodometric Analysis of *o*-Nitrobenzeneseleninic Acid

By Olav Foss

o-Nitrobenzeneseleninic acid has been found to react with thiosulfuric acid as follows

$$o\text{-}O_2NC_6H_4Se(O)OH + 3S_2O_3^{--} + 3H^+ = o\text{-}O_2NC_6H_4SeS_2O_3^{-} + S_4O_6^{--} + 2H_2O$$

The reaction is rapid and quantitative. The reaction product, *o*-nitrobenzeneselenenyl thiosulfate, has previously been isolated as a potassium salt by the reaction of *o*-nitrobenzeneselenenyl bromide with potassium thiosulfate,[1] and is also formed in reactions of various *o*-nitrobenzeneselenenyl sulfur compounds with thiosulfate.[1] It forms yellowish green, stable solutions. In neutral and acid solutions it is indifferent to iodine and does not interfere with iodine–thiosulfate titrations carried out in the same solutions. Hence the above reaction may be utilized for the iodometric analysis of *o*-nitrobenzeneseleninic acid, excess of thiosulfate being back-titrated with iodine. The following procedure may be employed.

To 12–20 mg. of *o*-nitrobenzeneseleninic acid dissolved in 25 ml. of water are added 5 ml. of 0.1 *N* sulfuric acid and then 20–30 ml. of 0.01 *N* sodium thiosulfate (5 ml. excess). After standing for two to three minutes at room temperature, starch is added, and the excess of thiosulfate is back-titrated with 0.01 *N* iodine.

Notice may be made to the analogous method of Norris and Fay[2] for the iodometric analysis of selenious acid, by means of the change

$$SeO_2 + 4S_2O_3^{--} + 4H^+ = Se(S_2O_3)_2^{--} + S_4O_6^{--} + 2H_2O$$

Experimental

The *o*-nitrobenzeneseleninic acid employed was prepared from the trichloride by hydrolysis,[3] and recrystallized from water until colorless.

0.1589 g. of the acid was dissolved to 250 ml. in water in a volumetric flask. Twenty-five ml. was pipetted out and 5 ml. 0.1 *N* sulfuric acid and then 25 ml. 0.01 *N* sodium thiosulfate (consuming 24.79 ml. of 0.01078 *N* iodine) were added. The time of standing was 2, 2, 5, 5, 8, 8 minutes. Amounts of 0.01078 *N* iodine then consumed: 5.95, 5.92, 5.92, 5.93, 5.92, 5.93 ml., respectively. Average: 5.93 ml., which gives 0.1585 g. of *o*-nitrobenzeneseleninic acid, *i.e.*, 99.7%.

Indifference of *o*-nitrobenzeneselenenyl thiosulfate to iodine. To 25 ml. of 0.01 *N* sodium thiosulfate were added 5 ml. 10% acetic acid, 5 ml. of starch solution, and (a) 20 ml. of water, (b) 20 ml. of 0.01 *M* potassium *o*-nitrobenzeneselenenyl thiosulfate. The solutions were then titrated with 0.01 *N* iodine. Amounts consumed: (a) 24.49, 24.50 ml. (b) 24.50, 24.50, 24.49 ml.

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(1) Foss, This Journal, **69**, 2236 (1947).

(2) Norris and Fay, *Am. Chem. J.*, **18**, 703 (1896); **23**, 119 (1900).

(3) Behaghel and Seibert, *Ber.*, **66**, 708 (1933).

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Mixed Crystal Formation in Linear Copolyesters

By C. S. Fuller

Slagle and Ott[1] showed that solidified mixes of normal aliphatic acids frequently exhibit a single X-ray spacing along the direction of the molecule axes in the mixed crystal. The purpose of this note is to point out that an analogous behavior occurs in copolymers in which the constituents are ethylene glycol dibasic acid residues of different chain lengths and, presumably, are randomly distributed along the long chain molecules.

A copolyester capable of being cold drawn into strong fibers was prepared by treating equal molar quantities of pure 10-, 11- and 12-membered aliphatic dicarboxylic acids with ethylene glycol. The X-ray fiber diagram of the copolymer (Fig. 1 (a)) is similar to that exhibited by many simple linear polyesters.[2] A mixed crystal is therefore indicated.

The average fiber period for the copolyester measures 17.83 Å. This value was obtained from the three strongest layer-line reflections (17.78, 18.00, 17.70). The fiber periods of the constituent ethylene polyesters prepared from the individual pure dibasic acids according to the same procedure are as follows

Ethylene decane 1-10 polyester	16.86 Å.
Ethylene undecane 1-11 polyester	36.32 (18.16 Å.)
Ethylene dodecane 1-12 polyester	19.40 Å.

The odd number of chain atoms in the 1-11 polyester causes a doubling of the fiber period. In addition, as the fiber pattern of Fig. 1b shows, the polar layers are perpendicular to the fiber axis unlike the even polyesters in which these planes are inclined to the axis.[3] It is noteworthy that (insofar as we can speak of polar layers in the copolymer) the pattern of the copolyester exhibits

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(1) Slagle and Ott, This Journal, **55**, 4396 (1933).

(2) Carothers and Hill, *ibid.*, **54**, 1579 (1932).

(3) Fuller and Frosch, *J. Phys. Chem.*, **43**, 323 (1939).