its surroundings. This apparatus, with its automatic temperature control system, makes it possible for the first time to hold sulfur in a calorimeter for long periods of time at virtually constant temperatures and observe the approach to equilibrium by observing the accompanying thermal effects. Many of the experiments described have involved waiting from 2 to 6 hr. before the rate of change of the calorimeter temperature reached the level of uncertainty.

The data obtained indicate the existence of a second stable "monoclinic" modification.

The heat capacity of the liquid at equilibrium is established, showing the λ-shaped maximum in detail. Differences from older data may be largely calorimetric, but the possibility remains that impurities may affect the shape of the heat capacity curve.

The measurements have been made with sufficient care to establish the values for the thermodynamic functions of sulfur between room temperature and the normal boiling point with an acccuracy acceptable for thermochemical calculations.

Acknowledgments.—The continual interest and encouragement of Professor W. J. Svirbely are gratefully acknowledged. Thanks are due to Mr. M. L. Reilly for the use of the computer code which he is developing for treating heat capacity data and to Mr. C. H. Hochgesang for constructing the container. The author is especially indebted to Dr. D. C. Ginnings for many valuable discussions regarding the vagaries of calorimetric and electronic apparatus.

WASHINGTON, D. C.

[CONTRIBUTION NO. 866 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Kinetics and Mechanism of the Periodate Oxidation of α-Diketones

BY V. J. SHINER, JR., AND C. R. WASMUTH[1]

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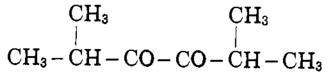
The rates of oxidation of diacetyl, diisobutyryl, benzil and camphorquinone by periodate solutions over a range of *p*H have been measured and correlated with the changes in concentration of the various ionized species of periodate present in these solutions and the separate rates of reaction of each of the periodate species with the α-diketones. The concentrations of the various species of periodate present in solution were determined spectrophotometrically using the general method of Crouthamel[6] with the important exception that the third stage of ionization is found to take place around *p*H 12.0 as indicated by a change in the optical density of the periodate solutions at 250 mμ in the *p*H range 11–13. The results are interpreted in terms of a nucleophilic attack of each of the six-coördinated periodate species on the carbonyl carbon atoms of the glycol to form a transient intermediate which undergoes spontaneous decomposition to the products, iodate and two molecules of carboxylic acid. The reaction rate is first order in periodate and first order in α-diketone over a fairly wide range of concentration and the rate of attack of the periodate increases as the degree of ionization increases.

A rather extensive body of work on the kinetics and mechanism of the oxidation of α-glycols by periodic acid has been accumulated through the efforts of several groups of authors[2] with the result that these reactions seem now to be fairly well understood. The evidence seems best explained in terms of the prior formation of a kinetically appreciable concentration of a cyclic complex through coordination of the oxygen atoms of the glycol with the iodine atom of the periodate. This complex, in the singly negatively charged state of ionization, then undergoes electronic rearrangement and decomposition into the products, iodate and two organic fragments containing new carbonyl groups.

The periodate oxidation of α-diketones however has received relatively little attention. The only kinetic observations reported have been by Clutterbuck and Reuter[3] who found that diacetyl was oxidized much more rapidly than benzil, and by Taylor, Soldano and Hall,[4] who reported that the oxidation of diacetyl proceeded *via* an initial fast reaction followed by a subsequent slower one, which showed a negative salt effect and a low activation energy. Because of its relationship to the glycol oxidation and because of the various possibilities for reaction between the several different species of both periodate and α-diketone that exist in solution, it seemed that a more thorough investigation of the α-diketone oxidation would be of interest. The present paper reports studies on the kinetics of the periodate oxidation of diacetyl (I), diisobutyryl (II), benzil (III) and camphorquinone (IV). Initial

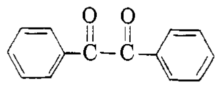
$CH_3COCOCH_3$

I

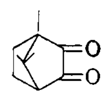


$$CH_3-\overset{CH_3}{\overset{|}{C}}H-CO-CO-\overset{CH_3}{\overset{|}{C}}H-CH_3$$

II



III



IV

kinetic studies indicated that the reactions were strictly second order, first order in total periodate concentration and first order in α-diketone, and that there was formed no kinetically detectable concentration of an intermediate complex. The kinetic studies then were extended to include measurements over a considerable range of *p*H to determine which of the species of periodate originating from the dissociation of the acid were reactive in the oxidation. The concentrations of the various per-

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(1) Abstracted in part from a thesis submitted by C. R. Wasmuth to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree.

(2) For detailed information on this reaction see G. J. Buist and C. A. Bunton, *J. Chem. Soc.*, 4580 (1957), and references cited therein.

(3) P. W. Clutterbuck and F. Reuter, *ibid.*, 1467 (1935).

(4) J. E. Taylor, B. Soldano and G. A. Hall, THIS JOURNAL, **77**, 2656 (1955).

iodate species were determined spectrophotometrically. The diketones benzil, diisobutyryl and camphorquinone, were found to behave as acids in strongly basic solutions and these equilibrium constants were determined for use in the correlation of the oxidation rate constants.

Results and Discussion

It has been shown by Clutterbuck and Reuter[3] that the reaction between diacetyl and periodic acid consumes one mole of each reactant and produces two moles of acetic acid. This stoichiometry and the second-order nature of the reaction in solutions of higher *p*H has been confirmed in the present work by measuring the one-half to three-quarter reaction times and the optical densities at the reaction end for several different concentrations of diacetyl and periodate. The results for such a series at *p*H 9.8 are given in Table I.

TABLE I

OXIDATION OF DIACETYL BY PERIODATE[a]

Concn., moles/l. × 10^{-4} Diacetyl	Periodate	$(t_{3/4} - t_{1/2})$[b] (sec.)	Infinity optical density at 222.5 mμ
1.13	1.01	54	0.158
1.07	1.01	61	.158
1.02	1.01	65	.172
0.96	1.01	60	.195

[a] Solutions at 24°, *p*H 9.8, ionic strength 0.2. [b] This is the difference in time between 75 and 50% completion of the reaction.

The absorption due to diacetyl and acetate at 222.5 mμ is negligible. The 0.158 optical density represents absorption due to the iodate product when all of the periodate is reduced. The optical density values higher than 0.158 represent incomplete reduction of the periodate. For second-order reactions the one-half to three-quarter reaction time for a given initial concentration of one reactant should be a maximum where the initial concentrations of the two reactants are equal. The table indicates that the longest reaction time with still essentially complete periodate reduction occurs with a diacetyl concentration to periodate concentration ratio near 1.02/1.01. Similar experiments for diisobutyryl at *p*H 11 indicated a 0.9/1 to 1/1 stoichiometry.

The order of the reaction was demonstrated in other cases by varying the initial concentration of the diketone where it was present in large excess and checking the constancy of the second-order rate constant. The data are listed in Table II. More general confirmation is shown by the fact that all the rate data taken with the DU spectrophotometer were successfully fitted to second-order rate equations.

TABLE II

EFFECT OF INITIAL DIKETONE CONCENTRATION ON SECOND-ORDER RATE CONSTANT

Diketone	Initial concn. (mole/l. × 10^4) Periodate	Diketone	*k* (l./mole/sec.)	*T*, °C.	*p*H
Diacetyl	4.5	226	0.098	0	1.1
	4.5	452	0.102	0	1.1
Diisobutyryl	0.75	4.14	5.9	22	11.6
	.75	2.07	6.0	22	11.6
Diisobutyryl	.75	4.14	0.38	22	8.4
	.75	8.12	0.38	22	8.4

We did not observe the initial fast oxidation of diacetyl reported by Taylor, Soldano and Hall.[4] Their method of rate measurement, which involved quenching of the reaction mixture in bicarbonate buffer, may have brought about simultaneous quenching and acceleration of the diacetyl oxidation, thereby producing an apparent initial fast rate.

It was observed that the *p*H changes had a marked effect on the rates of oxidation of the diketones. This would be expected because of the accompanying change in the degree of ionization periodate. Crouthamel and co-workers[5,6] detected the following equilibria in periodate solutions and determined the various equilibrium constants

$$H_5IO_6 \rightleftarrows H_4IO_6^- + H^+$$

$$H_4IO_6^- \rightleftarrows IO_4^- + 2H_2O$$

$$H_4IO_6^- \rightleftarrows H_3IO_6^{=} + H^+$$

$$H_3IO_6^{=} \rightleftarrows H_2IO_6^{\equiv} + H^+$$

The concentrations of H_5IO_6, IO_4^- and $H_3IO_6^{=}$ in the periodate solutions used in this work were determined using the observed absorption intensities and the extinction coefficients reported by Crouthamel, *et al.*,[6] for these species at 222.5 mμ. However, as shown in Table III, an additional important change in the absorption intensity of periodate solution has been observed to be centered about 250 mμ as the *p*H of the solutions changes from 10.5 to 13.5.

TABLE III

MOLAR EXTINCTION COEFFICIENTS OF POTASSIUM PERIODATE AT 22° (UNITS ARE ε × 10^{-4})

(mμ)	*p*H 9.9	*p*H 11.6	*p*H 12.6	*p*H 13.6
228	0.456	0.460	0.492	0.491
231	.424	.421	.440	.438
233	.409	.404	.408	.399
235	.396	.388	.380	.374
250	.299	.282	.204	.170

This variation is taken to be the result of the third ionization stage and the difference in absorption between $H_3IO_6^{=}$ and $H_2IO_6^{\equiv}$. A fall off in absorption at 222.5 mμ for periodate solutions of *p*H greater than 13.5, observed by the earlier workers,[6] was attributed by them to the third ionization stage. In this work it was found that this decrease is not coincident with a proportionate decrease at wave lengths higher than 222.5 but rather is coincident with the shifting of the absorption maximum toward higher wave lengths and cannot with any certainty be attributed to a simple change in ionization level. The explanation of this behavior at high *p*H's must therefore await further study. The data in Table IV show that Beer's law is followed by periodate solutions of *p*H 10.3 and 12.5 at 250 mμ. This work then indicates that the pK_a for the third stage of ionization of periodic acid is approximately 12.0 instead of 14.3 as previously reported.[6] This is in much closer agreement with the value of 11.0 calculated

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

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

using the semi-empirical expression derived by Ricci.[6,7]

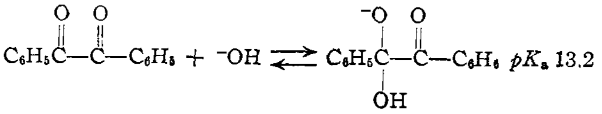
TABLE IV

ABSORPTION OF AQUEOUS POTASSIUM PERIODATE AT 250 mμ

*p*H	Cell thickness, cm.	Optical density	Relative concn.
10.5	1.007	0.683	10
10.5	10.002	.687	1
12.5	1.007	.515	10
12.5	10.002	.490	1

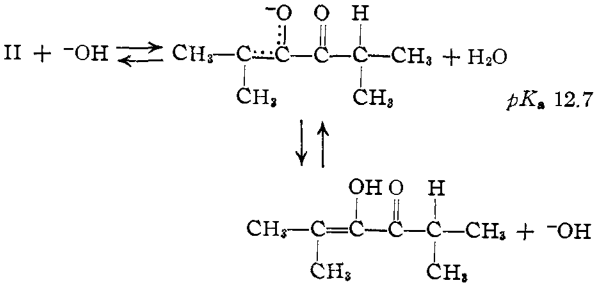
The absorption spectral curves for the different periodate species are indicated in the figure.

The correlation of periodate oxidation rates of the diketones in solutions of high *p*H is complicated by the partial conversion of these compounds into their conjugate bases. The occurrence of these phenomena can be observed and the pK_a values of the diketones can be calculated by the examination of the associated ultraviolet spectral changes. Benzil in neutral solution has a λ_{max} at 264 mμ and a molar extinction coefficient (ϵ) of 22,000. In strongly basic aqueous solutions this peak is lost and a new one with λ_{max} at 251 mμ and ϵ of 8,900 appears. This change can be associated with a pK_a for the benzil solution of about 13.2. The basic form of benzil is probably the singly ionized benzil monohydrate



$$C_6H_5\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-C_6H_5 + {}^{-}OH \rightleftarrows C_6H_5\underset{OH}{\underset{|}{\overset{{}^{-}O}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-C_6H_5 \quad pK_a\ 13.2$$

An analogous compound is evidently formed in strong base by camphorquinone which in neutral solution has an absorption peak at 460 mμ with a molar extinction coefficient of 39. This latter value drops to 0.0 in strong base and a new peak at 324 mμ with a molar extinction coefficient of 120 appears. The pK_a associated with this change is 13.4. Enolate formation with camphorquinone would be a violation of Bredt's rule. In basic solution diisobutyryl has an absorption maximum at 319 mμ with a molar extinction coefficient of 900. In neutral solution the extinction coefficient at this wave length is 3. The pK_a associated with this change is 12.7. On acidification of the strongly basic solution of diisobutyryl a strong band (ϵ > 2,000) appears at 270 mμ. This band decreased in intensity by more than 90% on standing overnight. A carbon tetrachloride extract made on such a solution immediately on acidification showed infrared absorption bands at 2.93, 6.02 and 6.14 μ. These bands are not shown by diisobutyryl itself and they disappear on standing. They must be due to the O–H, C═O and C═C stretching vibrations, respectively. Therefore the conjugate base of the diisobutyryl must be the enolate ion. This may be in equilibrium with an undetermined but probably small amount of the singly ionized monohydrate.



$$\begin{gathered}\mathrm{II} + {}^{-}OH \rightleftarrows CH_3-\underset{CH_3}{\underset{|}{C}}\cdots\overset{{}^{-}O}{\overset{\vdots}{C}}-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_3 + H_2O \qquad pK_a\ 12.7\\ \downarrow\uparrow\\ CH_3-\underset{CH_3}{\underset{|}{C}}=\overset{OH}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-CH_3 + {}^{-}OH\end{gathered}$$

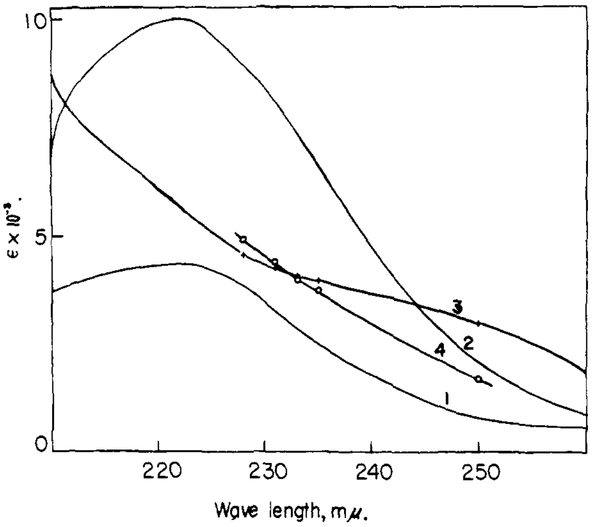
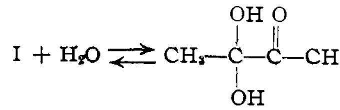


Fig. 1.—Extinction coefficients *vs.* wave length for periodate solution at several *p*H's: 1, *p*H 1.0, ~75% of periodate is H_5IO_6; 2, *p*H 6.5, ~97% of periodate is IO_4^- + 3% $H_4IO_6^-$; 3, *p*H 10.2, ~100% of periodate is $H_3IO_6^{=}$; 4, *p*H 13.6, ~100% of periodate is $H_2IO_6^{\equiv}$. Marked points taken from Table III, other data from ref. 5.

Forster[8] has pointed out that visible spectral data indicate that diacetyl is largely hydrated in aqueous solution. This form can be concluded to be mainly the monohydrate since Petuely and Meixner's[9] spectrum of aqueous diacetyl shows a band at 282.5 mμ which is typical of a carbonyl group.

Observations reported in the Experimental section, on the relative intensities of the absorption bands of aqueous diacetyl at 29 and 42° indicate, under certain reasonable approximations, that the hydration of diacetyl is exothermic to the extent of about 5 kcal./mole. Diacetyl undergoes rapid condensation in aqueous solutions of higher *p*H so that there are no long-lived basic forms.



$$\mathrm{I} + H_2O \rightleftarrows CH_3-\underset{OH}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-CH_3$$

The second-order rate constants for the oxidation of these diketones by periodate at several different *p*H's each are listed in Table V. On the assumption that the rate of the reaction at *p*H's 7.6 and 8.4 was due entirely to $H_3IO_6^{=}$, the rate of reaction of this species with each of the diketones was calculated and tabulated as k_2. The second-order rate constants for the reactions with $H_2IO_6^{\equiv}$ (k_3) were calculated at higher *p*H's with corrections made for the concentration of the diketone in the basic form and for the rate of reaction and concentration of $H_3IO_6^{=}$. The agreement between the duplicate

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[7] J. E. Ricci, THIS JOURNAL, **70**, 109 (1948).

[8] L. S. Forster, *ibid.*, **77**, 1417 (1955).

[9] F. Petuely and N. Meixner, *Monatsh.*, **84**, 1061 (1953).

TABLE V

OXIDATION OF DIKETONES BY AQUEOUS PERIODATE AT 22°[a]

Diketone	Initial concn. (mole/l. × 10^4) Diketone	Initial concn. (mole/l. × 10^4) Periodate	pH[b]	% $H_3IO_6^-$	% $H_2IO_6^{\equiv}$	$k_{obsd.}$[c]	k_2[d]	k_3[e]
I	1.01	1.01	10.0	100		300	300	
	1.00	1.00	8.2	58		186	320	
	1.00	1.00	7.2	16		43	270	
II	8.12	0.75	7.6	28.5		0.194	0.68	
	8.12	.75	8.4	71		0.381	0.54	
	2.07	.75	11.6	56.6	43.4	6.0		14
III	0.200	1.00	7.6	28.5		0.59	2.1	
	.200	1.00	8.4	71		1.52	2.1	
	.200	1.00	11.6	60	40	11.7		27
	.200	1.00	12.3	23	77	17.5		25
IV	4.00	0.75	7.6	28.5		0.159	0.56	
	4.00	.75	8.4	71		0.346	0.49	
	2.00	.75	11.6	56.6	43.4	7.6		17
	2.00	.75	12.3	22.5	77.5	13.8		19

[a] Ionic strength adjusted to 0.25 except for the diacetyl experiments which were done at ionic strength 0.20. [b] pH values are approximate. Periodate species concentrations were determined spectrophotometrically. [c] Units for k are l./mole/sec. [d] Calculated rate for oxidation by $H_3IO_6^{=}$. [e] Calculated rate for oxidation by $H_2IO_6^{\equiv}$.

values of the constants obtained is generally within the expected experimental error.

In Table VI are shown the observations on the rate of diacetyl oxidation in acidic aqueous periodate solutions at a series of different pH's. The calculated values for k were obtained by using $k_2 = 350$, $k_1 = 0.39$ and $k_0 = 0.74$ and the concentrations of the different periodate species calculated from spectrophotometrically measured ionization constants and the various observed pH values. The rate constant for the reaction with the doubly ionized periodate used here was somewhat larger (350) than that calculated from the results given in Table V probably due to the slight errors in pH measurement in the acid solutions.

TABLE VI

OXIDATION OF DIACETYL BY AQUEOUS PERIODATE[a]

(T = 22°, ionic strength = 0.25)

pH	% H_5IO_6	(% IO_4^- + % $H_4IO_6^-$)	% $H_3IO_6^{=}$	k[b] Obsd.	k[b] Calcd.
5.40	..	99.8	0.245	1.25	1.25
4.74	..	99.9	.054	0.63	0.58
4.30	0.3	99.7	.020	.46	.46
3.63	1.3	98.7	.004	.37	.41
2.21	25.2	74.8	...	.48	.48
1.21	77.1	22.9	...	.65	.66

[a] Concentrations were diacetyl, 0.97 × 10^{-3} and KIO_4, 0.80 × 10^{-4} mole/l. [b] Units of k are l./mole/sec.

The rates of the periodate oxidation of the α-diketones have thus been correlated fairly well with the assumption that the rate can be expressed as

$$\text{rate} = (\text{diketone})\ \{k_0(H_5IO_6) + k_1[(H_4IO_6^-) + (IO_4^-)] + k_2(H_3IO_6^{=}) + k_3(H_2IO_6^{\equiv})\}$$

The constants calculated are summarized in Table VII.

If the k_1 value for diacetyl is assumed to be due to oxidation by the total singly charged periodate present (mostly IO_4^-) then the constant is 0.39 l./mole/sec. However, if it is assumed that the only active singly negatively charged form is $H_4IO_6^-$, then the rate constant for this species is 13.3 l./mole/sec. This latter value fits in with the reasonable assumption that it is only the periodate species with six oxygen atoms that are active in the oxidation and that the activity of the species increases fairly regularly with their basicity. This assumption is also favored by the observation that at 0° the rate of oxidation of diacetyl increases in the ratio 1.0:1.7:2.8 as the pH increases from 1 to 3 to 4. Since at 22° the rates actually decrease through these pH changes, this would indicate that the activation energy is higher for oxidation by H_5IO_6 than for oxidation by IO_4^- if the latter were the active singly charged species. The more reasonable assumption that $H_4IO_6^-$ is the only active singly charged species gives an activation energy for its reaction more nearly comparable to that for H_5IO_6.

TABLE VII

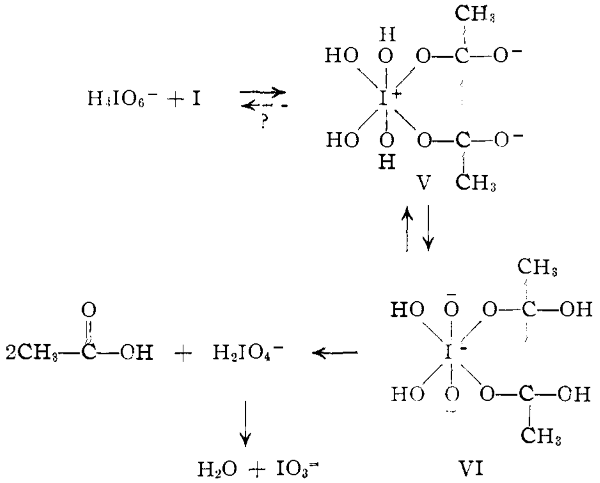
SUMMARY OF RATE CONSTANTS[a] FOR OXIDATION OF α-DIKETONES BY PERIODATE SPECIES

Diketone	k_0	k_1	k_2	k_3
I	0.74	0.39(13.3)[b]	350	
II			0.61	14
III			2.1	26
IV			0.52	18

[a] Units are l./mole/sec. [b] The value 0.39 is obtained by assuming all of the singly negatively charged periodate to be active. If one assumes that IO_4^- is inactive and $H_4IO_6^-$ is active the k for the latter is 13.3.

The experiments on the effect of buffer concentration show that at 0° and pH 1.8 the diacetyl oxidation by periodate is not catalyzed significantly by acetic acid. However, at pH 4.5 a large increase in the sodium acetate–acetic acid buffer concentration at constant ionic strength gave an appreciable increase in oxidation rate indicating either general acid or general base catalysis. In view of the absence of an effect by acetic acid at pH 1.8 this is probably acetate ion catalysis. However, the magnitude of this effect indicates that such acetate ion catalysis would account for only about 2% of the value of any k in the experiments whose results are summarized in Table VI. This is because the buffer concentrations were very low in these latter experiments. Other data indicate similarly negligible catalytic effects due to phosphate buffer in the experiments summarized in Table V.

In the treatment given it has been assumed that the reaction could be represented by a summation of bimolecular reactions each involving one molecule of periodate in one of its stages of ionization and one molecule of diketone. The data have been fitted with this assumption to within the experimental error. However, there is no kinetic proof that some of the reactions attributed to the more highly ionized forms are not actually reactions of the less highly ionized forms catalyzed by the appropriate number of hydroxide ions. The reaction is pictured as proceeding by a nucleophilic attack of the periodate oxygen atoms on the carbonyl carbon atoms of the α-diketone to form a cyclic complex as in the example



Even though the reaction proceeds rather rapidly and no kinetically detectable concentration of complex is formed, there should certainly be time enough for proton exchange equilibrium between V and VI to be established and VI would certainly be the most stable because of the greater acidity of at least the first three hydrogens of paraperiodic acid over the hydrogens of the glycol hydrate type. However, V should decompose more readily than VI because the former process liberates directly the resonance energy of the two carboxylate groups formed while the latter one would not. Therefore, it does not seem possible to make a choice for the important complex. These complexes should be considered as well to be in equilibrium with similar ones in which one or more additional hydrogen ions have been removed. These latter complexes might be formed also directly from the higher ionized forms of periodic acid and the diketone. Since all of the proton shifts must be assumed to be very rapid, it cannot be said which of the periodate species attack the diketone directly if the first step is considered to be reversible. Nor can it be said which of the complexes decompose directly to the product. It might be any or all of the *a priori* possibilities in each case. The decomposition of one or more of the complexes might reasonably be expected to be subject to general base catalysis which, if the first step of the reaction were reversible, would be reflected in general base catalysis of the over-all reaction. These mechanisms all differ from that which obtains for the periodate oxidation of α-glycols in that in the former the coördination proceeds through the oxygens of the periodate which are eventually incorporated into the organic products and in the latter the coördination is through the glycol oxygen atoms which remain attached to the organic products.

The usefulness of the observation that the periodate oxidations of α-diketones proceed more readily in strongly basic solutions is severely limited by the decreasing solubility of all known periodates in increasingly basic solutions.

Experimental

Compounds Used.—Commercial benzil was recrystallized from carbon tetrachloride. *dl*-Camphorquinone was prepared by the selenium dioxide oxidation of *dl*-camphor[10] and recrystallized to m.p. 198–199.5° from low boiling petroleum ether. Commercial diacetyl was purified by fractional distillation, b.p. 87.5–88.5° (740 mm.) in a spinning band column. The acyloin condensation of ethyl isobutyrate[11] gave a product, b.p. 59°–62° (6 mm.) which was oxidized by copper acetate[12] to diisobutyryl. This compound was also purified by distillation in the spinning band column, b.p. 144–145° (740 mm.).

Rate Measurements at 0°.—One hundred ml. of buffer solution and 25 ml. of potassium periodate solution were pipetted into a 500-ml. volumetric flask, and 5 ml. of diacetyl solution was added to start the reaction. At appropriate time intervals, 10-ml. aliquots were pipetted from the reaction mixture and drained into 180 ml., covered, electrolytic beakers containing 15 ml. of 0.7 *N* sulfuric acid, 5 ml. of 4% potassium iodide solution and a few grams of solid carbon dioxide. The samples were titrated for iodine with 0.0015 *N* sodium thiosulfate solution using a dead-stop end-point method.[13] The solutions used in the kinetic studies were thermostated before and after mixing in a 0° constant temperature bath.

Rate Effect of Buffer Concentration.—Two sets of kinetic runs were done at 0° in the manner described above to determine the extent of acetate and acetic acid catalysis of the diacetyl oxidations.

The first set consisted of two kinetic runs done in solutions having identical concentrations of perchloric acid (*p*H 1.8), potassium periodate (0.00059 *M*) and diacetyl (0.00152 *M*). The solution for one of these runs contained acetic acid (0.19 *M*) and that for the other did not. The rate constants obtained were 0.16 and 0.17 l./mole/sec., respectively, indicating the absence of acetic acid catalysis.

The second set consisted of three runs. Each of the three reaction solutions was 0.000595 *M* in potassium periodate and 0.000748 *M* in diacetyl. The solution for the first run was also 0.41 *M* in acetic acid and 0.35 *M* in sodium acetate while that for the second was 0.082 *M* in acetic acid and 0.070 *M* in sodium acetate. The solution for the third run was identical to that for the second except that the ionic strength was adjusted to 0.35 by the addition of sodium perchlorate. The rate constants for the three runs were 1.9, 0.64 and 0.75 l./mole/sec., respectively, indicating significant catalysis by the acetate buffer and a rather small salt effect.

Rate Measurements at Room Temperature.—These reactions were followed with a Beckman DU spectrophotometer or, in the case of the rapid reactions, with a Beckman DK spectrophotometer. The slow reactions were started by adding 5 ml. of diketone solution to a 100-ml. volumetric flask containing 50 ml. of buffer solution and 5 ml. of potassium periodate solution. The stock solutions of all the diketones, except diacetyl, were made up in 50% aqueous *t*-butyl alcohol. Samples of the reaction mixtures, removed at appropriate intervals, were measured for optical density at 264 mμ in the case of benzil and at 222.5 mμ for the other diketones. The change in optical density was proportional to the change in concentration of the benzil or the potassium periodate, and from this information the second-order rate constants were calculated. The optical density at the start of each reaction was determined by extrapolation. Because

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of the rapidity of the reactions and the low temperature coefficients, the reaction solutions were not kept in thermostated baths. The temperature of the room was controlled to within 0.5° by air-conditioning.

The rates of the rapid reactions of diacetyl in solutions of high *p*H were measured with a DK spectrophotometer. A sample of the reaction mixture was placed in the instrument immediately after mixing and the recorder was then turned on. The initial optical densities were calculated from optical density measurements of separate solutions of each of the reaction mixture components. The recorder speed was two inches per minute. The rates were then calculated from the time required for the reaction to proceed a definite fraction toward completion, such as the one-half reaction time to the three-quarter reaction time.

The *p*H of the reaction mixture was adjusted with perchloric acid for low values of *p*H, with sodium acetate and acetic acid for *p*H 3–5, with sodium dihydrogen phosphate and sodium hydroxide for *p*H 6–10 and with potassium hydroxide for *p*H 11 and above. Sodium perchlorate was used to adjust ionic strength for solutions of *p*H 1–10 and potassium sulfate for solutions of *p*H 11 and above.

The concentrations of the various ionized species of periodate were determined spectrophotometrically. The relative amounts of the species with charge −1 and 0 were determined by measuring the optical density of the buffer solution at 222.5 mμ and comparing this with the extinction coefficient of the uncharged periodate as reported by Crouthamel[5,6] and the extinction coefficient of the total singly-charged periodate as determined for a solution containing all singly-charged periodate. The relative amounts of singly and doubly-charged periodate were determined in a similar fashion at 222.5 mμ using a solution of *p*H 10.3 as a standard for the doubly-charged ion. The relative amounts of doubly and triply charged periodate were obtained at 250 mμ using solutions of *p*H 10.3 and 13.6 as standards representing all charge type −2 and −3, respectively.

Ionization constants for the diketones were obtained by spectrophotometric measurements at 264 mμ for benzil, 324 and 460 mμ for camphorquinone and 319 mμ for diisobutyryl. *p*H-measurements were taken with a Leeds and Northrup Model 7664 *p*H meter with calomel and glass electrodes.

Test for Enolization of Camphorquinones.—A 404-mg. sample of camphorquinone was dissolved in 4.035 g. of absolute alcohol to which was added 0.172 g. of sodium hydroxide dissolved in 5.138 g. of 40% deuterium oxide, and the solution was allowed to stand for 20 minutes. The solution was extracted with anhydrous ether and the extracts were dried with potassium carbonate. The ether was then evaporated with an aspirator and the product was recrystallized from a 60–99° fraction of petroleum ether. The camphorquinone was oxidized in a combustion train and the resulting water had a D_2O content of 0.2 mole %.

Preparation of Diisobutyryl Enol Extract.—A 520-mg. sample of diisobutyryl was dissolved in 20 ml. of 95% alcohol. Twenty ml. of water and 40 ml. of an aqueous solution of 1.6 g. of sodium hydroxide were added and, after mixing, 60 ml. of 1.2 *N* HCl was introduced. The solution was then immediately extracted with carbon tetrachloride. The extracts were combined and washed with 0.12 *N* HCl. The extracts was then dried with magnesium perchlorate and partially evaporated with the aspirator. After filtering, the infrared absorption spectrum was recorded on a Perkin-Elmer model 21 infrared spectrophotometer.

Heat of Hydration of Diacetyl.—The extinction coefficient of aqueous diacetyl at 409 mμ is 5.6 at 29° and 7.1 at 42°. If one assumes that (1) the extinction coefficient of 20 for this band observed for diacetyl in non-aqueous solution is characteristic of the diketo form and would obtain for this form in aqueous solutions, (2) that only the diketo form and the mono-hydrated form of diacetyl are present in aqueous solution and (3) that the extinction coefficient of the mono-hydrated form in aqueous solution at 409 mμ is zero it is possible to calculate approximately the degree of hydration at each of the above temperatures and a heat for the hydration process. The heat of hydration is approximately 5 kcal./mole. Diacetyl is approximately 72 and 65% hydrated at 29 and 42°, respectively.

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Kinetics of Three-compound Equilibrations. I. The Isomerization of Cymene[1]

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This work was carried out in order to study the kinetics of three-compound equilibrations and to aid in elucidating the mechanism of the isomerization of isopropyltoluene. The isomerization was assumed to proceed by the reaction pattern shown below, which yields the integrated rate equations: $O = O^* + Ae^{-\beta\tau} + Be^{-\beta\tau}$ and $P = P^* + Ce^{-\alpha\tau} + De^{-\beta\tau}$, where τ is a function of time, O and P are the *o*- and *p*-cymene concentrations, respectively, O^* and P^* are the *o*- and *p*-cymene equilibrium concentrations, respectively, α and β are constants determined by the set of rate constants and A, B, C, D are constants determined by the initial concentrations. Dilute solutions of five cymene isomer distributions in toluene were isomerized at 0° with small quantities of aluminum chloride. In each case samples were taken periodically, the toluene distilled off and the residue analyzed by infrared. The isomer distributions obtained are in excellent agreement with the following relative rates: $k_{om} = 45.8$, $k_{mo} = 1$, $k_{mp} = 2.4$, $k_{mp} = 5.5$, $k_{po} = 1$, $k_{op} = 19.9$. These relative rates prove that, although the mechanism for the isomerization of xylenes appears to be an intramolecular 1,2-shift, the mechanism for the isomerization of cymenes is not an intramolecular 1,2-shift.

Introduction

According to the literature at present, alkylbenzenes isomerize by intramolecular 1,2-shifts. Two independent studies indicate that the mechanism for xylene isomerization is an intramolecular 1,2-shift.[2,3] A similar mechanism has been proposed by Schlatter for the isomerization of 1,3-dimethyl-2-isopropylbenzene to 1,3-dimethyl-4-isopropylbenzene,[4] and an intramolecular mechanism has been proposed for the isomerization of *n*-propyl-β-C^{14}-benzene to *n*-propyl-α-C^{14}-benzene.[5]

The xylene isomerization kinetics were studied using molar quantities of $HF \cdot BF_3$[2] and using molar quantities of $AlBr_3 \cdot HBr$ in toluene solution.[3] The use of molar quantities of catalyst resulted in homogeneous reaction mixtures, so that absolute rates could be determined; and also resulted in isomerization to 100% *m*-xylene, so that the kinetics would not be complicated by the isomerization of the *m*-xylene formed.

In the present work the isomerization of cymenes was studied as a three-compound equilibration involving six rate constants. The reactions were run

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