188. *The Kinetics of Halogen Addition to Unsaturated Compounds. Part XIII. αβ-Unsaturated Ketones and Quinones.*

By H. P. Rothbaum, I. Ting, and P. W. Robertson.

The velocities of chlorine addition in the presence of sodium acetate (electrophilic rate), and of bromine addition with different amounts of added sulphuric acid (nucleophilic rate), to benzylideneacetophenone and its *p*-methyl and *m*-nitro-derivatives have been measured in acetic acid solution. The theoretical interpretation of these results is discussed. Whereas a 1 : 4-diketone, such as Ph·CO·CPh:CH·COPh, shows very low electrophilic and nucleophilic rates, quinones by the acid-catalysed mechanism add one molecule of bromine very rapidly, and the second molecule with extreme slowness. This is in accord with the previous finding that a nucleophilic process which involves a structure with adjacent positive polarities has a low rate for bromine addition (cf. Part IX, *J.*, 1945, 892).

The kinetics of halogen addition to αβ-unsaturated ketones have hitherto been little investigated. Ralls (*J. Amer. Chem. Soc.*, 1940, **62**, 3485) has measured the rates of bromine addition, in the presence of an equivalent amount of iodine, to $CHPh{:}CH{\cdot}CO{\cdot}C_6H_4Br(p)$ in acetic acid and carbon tetrachloride solution. A novel instance of steric hindrance is shown by the oxime of this ketone, the *cis*-stereoisomer adding bromine at a slower rate than the *trans*-compound.

Part VIII of this series (*J.*, 1945, 888) deals with the kinetics of chlorine and bromine addition to αβ-unsaturated aldehydes. These compounds in acetic acid solution show acid-catalysed nucleophilic halogen addition; the reactions are insensitive to light, the rates

are reduced by adding water to the solvent, and bromine addition is in general more rapid than chlorine addition. With regard to constitutional effects, the influence of substituents is usually in the reverse order to that found for electrophilic reactions. An investigation of halogen addition to the related ketones, CHR:CH·COR′, is possible when R′ is a radical such as phenyl or *tert.*-butyl, which does not permit halogen replacement. The present investigation deals chiefly with the kinetics of chlorine and bromine addition to benzylideneacetophenone, and its derivatives with a substituent in one of the phenyl groups. As relative to the rate of bromine addition the electrophilic rate for chlorine is high, and the nucleophilic rate is low, the velocity of chlorine addition (in the presence of sodium acetate to eliminate any acid-catalysed nucleophilic addition) is a measure of the electrophilic reaction, whilst bromine addition in the presence of acid proceeds by the nucleophilic mechanism. In the following table, such electrophilic and nucleophilic rates are shown for CHPh:CH·COPh and certain related compounds. The measurements were made in acetic acid solution at 24°, reactants M/80.

Compound.	CHPh:CH·CHO.	CHPh:CH·COPh.	CHPh:CH·CO_2Et.
k_2 (Cl_2, M/80-NaOAc)	1·8	61	10·0
k_2 (Br_2, M/80-H_2SO_4)	27	32	0·013 *

* Corrected by subtraction of electrophilic rate.

It will be noted that benzylideneacetophenone adds chlorine more rapidly than ethyl cinnamate, despite the fact that, as far can be judged from nucleophilic reactivity, the benzoyl group is more strongly electron-attracting than the carbethoxy-group. A similar difference is found for the corresponding *m*-nitro-compounds, the rates for chlorine addition in acetic acid at 24° being: *m*-NO_2·C_6H_4·CH:CH·COPh, $k_2 = 0{\cdot}23$; *m*-NO_2·C_6H_4·CH:CH·CO_2Et, $k_2 = 0{\cdot}011$. Thus the importance of polarizability influences in halogen addition, as envisaged by Ingold and Ingold (*J.*, 1931, 2354), is again exemplified. When electrophilic reactivity is required by the reagent, the phenyl group (in benzoyl) appears to be more polarizable than the ethoxy-group (in carbethoxy-), as is shown also by the rates of second-order chlorination of *p*-RO·C_6H_4X, where for X = COPh and CO_2Et, the relative rates are 287 and 189 respectively (Bradfield and Jones, *Trans. Faraday Soc.*, 1941, **37**, 743).

With reference to the nucleophilic reactions, both cinnamaldehyde and benzylideneacetophenone should add bromine at a considerably faster rate than ethyl cinnamate (as is experimentally found), since aldehydes and ketones have the normal nucleophilic reactivity, which esters do not possess. But whereas an aldehyde such as R·CHO is more highly reactive than a ketone, R·COPh, the rates of nucleophilic bromine addition to the cinnamaldehyde and benzylideneacetophenone do not differ greatly. Similarly, the rates with HBr_3, although too rapid for accurate measurement, are approximately the same [k_2 ($\frac{1}{4}$ mol. HBr), *ca.* 300]. A dual effect is here in operation. The replacement of the aldehyde hydrogen by phenyl increases the basicity, aiding the first stage of the acid-catalysed reaction, but the benzoyl group has a smaller electron-attracting power than the aldehyde group, and this is unfavourable to the second stage, which involves a nucleophilic attack on the positive β-carbon atom of the system.

The rates of electrophilic chlorine addition to compounds of the types C_6H_4X·CH:CH·COPh and CHPh:CH·CO·C_6H_4X are given in the following table, the measurements being made in acetic acid at 24°, reactants M/80, sodium acetate M/40.

(I) Ph·CH:CH·COPh	$k_2 = 61$	(V) *m*-NO_2·C_6H_4·CH:CH·COPh	$k_2 = 0{\cdot}23$
(II) Ph·CH:CH·CO·C_6H_4Me(*p*)	$k_2 = 61$	(VI) *p*-ClC_6H_4·CH:CH·COPh	$k_2 = 23$
(III) Ph·CH:CH·CO·C_6H_4·NO_2(*m*)	$k_2 = 15$	(VII) *p*-ClC_6H_4·CH:CH·CO·CMe_3	$k_2 = 36$
(IV) *p*-MeC_6H_4·CH:CH·COPh	$k_2 = ca.$ 800		

The effect of substituents in the benzoyl group is not large. The powerfully electron-demanding nitro-group reduces the rate, but only by a factor of 4 (III); a methyl group appears to have no effect on the rate (II). On the other hand, the influence of substituents in the second phenyl group (IV and V) is considerable, the methyl group increasing and the nitro-group reducing the rate. Such a difference may be partly attributable to the fact that electron-donor groups activate the β-carbon atom of the ethylenic system; in the above compounds, attack of halogen is α to the COR′ group, and therefore substituents in R (of R·CH:CH·COR′) will have a greater influence on the rates of addition than substituents in R′.

The following table gives the relative rates of chlorine addition for the substituted ketones examined in this paper and the corresponding cinnamic acids examined in Part IX (*J.*, 1945, 891).

	X = *p*-Me.	H.	*m*-NO_2.
C_6H_4X·CH:CH·COPh	13	1	0·0038
C_6H_4X·CH:CH·CO_2H.....	16	1	0·0017

With X = Cl (VI) there is in operation the normal dual effect, this substituent aiding the electrophilic mechanism by a tautomeric shift and acting reversely by induction. In general, the second effect tends to predominate in reactions that require a flow of electrons to the point of attack, and in this series of compounds the *p*-chloro-derivative reacts at about one-third of the rate of the unsubstituted compound.

Compounds (VI) and (VII) permit a comparison of the influence of the benzoyl and the pivaloyl group in determining the electrophilic rate. As ketones of the type R·CO·CMe_3 are considerably more reactive than R·CO·Ph, the relative rates of chlorine addition should therefore be (VII) > (VI). This is the experimental order, although a greater difference in reactivity was to be expected, if the electron-attracting power of the group COR′ was the sole determining factor.

The next table gives the rates of bromine addition (as bimolecular coefficients) to the substituted benzylideneacetophenones under various conditions, the measurements being made in acetic acid at 24° reactants M/80.

	NaOAc, M/40.	No catalyst.	H_2SO_4, M/40.	H_2SO_4, M/10.	H_2SO_4, M/5.
(I) Ph·CH:CH·COPh	0·33 *	15	35	47	50
(II) Ph·CH:CH·CO·C_6H_4Me(*p*)	0·33	16	29	29	—
(III) Ph·CH:CH·CO·C_6H_4·NO_2(*m*)	0·22	4	13	22	28
(IV) *p*-MeC_6H_4·CH:CH·COPh	7·8	64	73	73	—
(V) *m*-NO_2·C_6H_4·CH:CH·COPh	0·09	7	40	53	61

* NaOAc, M/160, k_2 = 0·31.

The influence of the base sodium acetate in the acid solvent is to eliminate the acid-catalysed nucleophilic reaction, so that the rates in the first column should be those of electrophilic bromine addition. The value for compound (V), however, is too high, as judged by the corresponding rates for electrophilic chlorine addition; it is possible therefore that acetic acid molecules, as well as hydrogen ions, may be effective to a slight extent in the nucleophilic reaction. A change in the sodium acetate concentration, examined for (I) (cf. table), has little influence on the rate of bromine addition. When sodium acetate is present, there is considerable sodium bromide formation, with the result that at lower concentrations of sodium acetate there is a sudden increase in rate (reactants M/80, sodium acetate M/320, at *ca.* 40% bromine absorption) owing to the change-over to the rapid acid-catalysed reaction. Lithium chloride is also a base in acetic acid solution, and likewise depresses the rate of bromine addition; *e.g.*, for (I), reactants M/80, k_2 (LiCl, 0·027M), 3·1; k_2 (LiCl, 0·081M), 3·6. These values are higher than those found in the presence of sodium acetate, in part because lithium chloride is a weaker base, and in part because it acts as a catalyst for the reaction.

The acid-catalysed reactions are considered to proceed according to the scheme (Part VIII, *loc. cit.*):

$$A + H^{\oplus} \underset{2}{\overset{1}{\rightleftarrows}} AH^{\oplus};\ AH^{\oplus} + Br_2 \underset{4}{\overset{3}{\rightleftarrows}} A,Br_2 + H^{\oplus};\ A,Br_2 \xrightarrow{5} ABrBr.$$

When the maximum rate with added acid is reached, $-d[Br_2]/dt = k_1k_3k_5[A][Br_2]/k_2k_4$.

Reference to the table reveals that the influence of sulphuric acid in increasing the rate is relatively greater for the weaker bases (III and V) than for the stronger bases (II and IV), for which the maximum rate is reached at a lower concentration of added acid. Benzylideneacetophenone (I) in this respect occupies an intermediate position, but, being a stronger base than cinnamaldehyde (Part VIII, *loc. cit.*), it shows a maximum rate with a lower concentration of acid. For the same reason the rates of (I) with perchloric acid (a stronger acid than sulphuric acid in acetic acid solution) are only slightly greater than with sulphuric acid (M/40-$HClO_4$, k_2 = 42; M/10-$HClO_4$, k_2 = 48), whereas for cinnamaldehyde the differences were greater.

With regard to the influence of substitutents in the phenyl groups of benzylideneacetophenone on the nucleophilic rates, our previous comparison of this compound and cinnamaldehyde has indicated that large differences were not necessarily to be expected for this kind of reaction. Here, similarly, dual opposing electronic effects are in operation, and, moreover, the extent of the acid catalysis varies from compound to compound, so that a choice of comparable conditions is involved. A further complication is that the reactions appear to be autocatalytic (see Experimental).

The rate of bromine addition to a 1 : 4-diketone, Ph·CO·CPh:CH·COPh, has also been measured in acetic acid at 24°, reactants M/80:

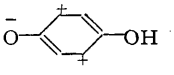
$$k_2\ (M/40\text{-NaOAc}) < 0{\cdot}0005;\ k_2\ (M/40\text{-}H_2SO_4) = 0{\cdot}048;\ k_2\ (M/10\text{-}H_2SO_4) = 0{\cdot}090$$

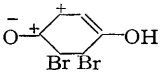
The very low electrophilic rate (in presence of sodium acetate) is due to the electron-abstraction by the two carbonyl groups. In the acid-catalysed nucleophilic reaction a low rate, *i.e.*, relative to that of benzylideneacetophenone, is to be expected, since the formation of the positive ion may set up an unfavourable structure with adjacent positive polarities, *viz.*, $\overset{-}{O}\cdot C\overset{+}{P}h\cdot\overset{+}{C}Ph\cdot CH{:}CPh\cdot OH$ (cf. Part IX, *loc. cit.*).

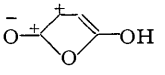
The *p*-benzoquinones, which have a similar unsaturated system, show likewise a low electrophilic rate of bromine addition, but on the other hand are characterised by very rapid acid-catalysed bromine addition in acetic acid solution. Thus the following values were obtained for thymoquinone in acetic acid at 24°, reactants M/80 :

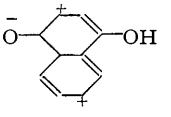
$$k_2\ (\text{M}/40\text{-NaOAc}) < 0{\cdot}01\ ;\ k_2(\text{M}/80\text{-}H_2SO_4) \sim 100$$

In a quinone, the formation of a positive ion can take place to give a structure (VIII) without the necessity of adjacent polarities, so that a high nucleophilic reactivity may be predicted. But even more reactive than the univalent ion could be the bivalent ion [formed from (VIII)] with its double positive charge, and it is possibly due to ions of this kind that quinones generally add bromine at such a high nucleophilic rate.


(VIII.)


(IX.)

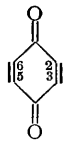

(X.)


(XI.)

When one molecule of bromine has been added to thymoquinone in acetic acid solution the reaction comes virtually to a stop, even in the presence of sulphuric acid, further absorption of bromine taking place with extreme slowness ($k_2 < 0{\cdot}0005$). This is in accord with theoretical expectation; in the dibromo-addition product of a quinone, part of the tautomeric system is blocked, and in the positive ion (IX) conditions are possible for adjacent polarities. At the same time the bromine atoms by their inductive effect tend to weaken the compound as a base and prevent salt formation, thus tending still further to reduce the nucleophilic rate of bromine addition. Similarly, maleic anhydride, which has a structure also leading to formation of adjacent polarities (X), adds bromine by the nucleophilic mechanism relatively slowly, and at the same time is characterised, owing to the considerable regression from the ethylenic system, by a very low electrophilic rate, as seen from the velocities in acetic acid at 24°, reactants M/80 :

$$k_2\ (\text{M}/40\text{-NaOAc}) < 0{\cdot}0005\ ;\ k_2\ (\text{M}/160\text{-}H_2SO_4) = 0{\cdot}0036\ ;\ k_2\ (\text{M}/10\text{-}H_2SO_4) = 0{\cdot}0082$$

Bromine addition to certain quinones has been measured in 1% aqueous acetic acid, in which solvent the rates of acid-catalysed addition are less than in acetic acid and become more conveniently measurable. The following relative velocities have been found, reactants M/80 + M/160-sulphuric acid :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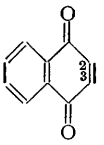
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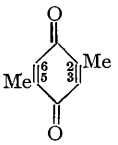
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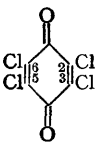
0.

In naphthaquinone the tautomeric system is not blocked, as is indicated by the formulation of one of the resonance structures of its ion (XI, above). Since positive-ion formation for naphthaquinone involves a greater change in the number of possible resonance structures than for benzoquinone, it can be assumed to be a weaker base, and for this reason its nucleophilic reactivity should be less. With OH in the 1 position, there is one point of nucleophilic attack (3) for naphthaquinone, but for benzoquinone two such points of attack (3 and 5); moreover, the fused benzene ring in the molecule should exert no polar influence on the 3-position. The rate for naphthaquinone should therefore be expected to be less than half that of benzoquinone.

The nucleophilic constitutional effects, *i.e.*, the reversal of the electrophilic order, observed for αβ-unsaturated acids (Part V) and for certain αβ-unsaturated aldehydes (Part VIII), but obscured in the αβ-unsaturated ketones (present communication), become again evident in the

case of *p*-xyloquinone. In this compound the methyl groups cause an electronic flow to the oxygen atoms, thereby aiding combination with hydrogen ions, the first stage of the reaction, but, at the same time, the methyl groups, by their inductive power, tend to neutralise the positive charges thus formed on the carbon atoms and so hinder the nucleophilic attack. This second effect predominates, and *p*-xyloquinone adds bromine by the nucleophilic mechanism more slowly than benzoquinone itself.

Tetrachlorobenzoquinone was found not to add bromine in acetic acid in the presence of sulphuric acid. As this compound reacts with hydroxyl ions to form chloranilic acid, partial positive charges are developed in the 2 : 5 (or 3 : 6) positions by resonance, but this in itself is not sufficient to cause nucleophilic bromine addition, which requires the actual formation of a positive ion. Tetrachlorobenzoquinone, however, by the inductive effect of its four chlorine atoms, becomes so weak a base that salt formation is virtually prevented, and it therefore cannot add bromine by the nucleophilic mechanism.

Experimental.

The benzylideneacetophenones used in this investigation were prepared from the corresponding derivatives of benzaldehyde and of acetophenone : Ph·CH:CH·COPh, m. p. 57° ; *p*-MeC_6H_4·CH:CH·COPh, m. p. 95° ; *m*-NO_2·C_6H_4·CH:CH·COPh, m. p. 143° ; Ph·CH:CH·CO·C_6H_4Me(*p*), m. p. 74° ; Ph·CH:CH·CO·C_6H_4·NO_2(*m*), m. p. 128° ; *p*-ClC_6H_4·CH:CH·COPh, m. p. 113° ; *p*-ClC_6H_4·CH:CH·CO·CMe_3, m. p. 84° ; Ph·CO·CPh:CH·COPh, m. p. 129°. In addition were used : *p*-benzoquinone, m. p. 116° ; *p*-xyloquinone, m. p. 124° ; thymoquinone, m. p. 45° ; 1 : 4-naphthaquinone, m. p. 124°.

The general technique was as described in Part VIII (*loc. cit.*), and here are the details of a typical rate measurement :

Ph·CH:COPh, M/80 + Br_2, M/80 + H_2SO_4, M/20 in HOAc, 24°.

(2 Ml. pipetted into 5% KI soln. and titrated with N/80-$Na_2S_2O_3$.)

Time (mins.)	0	0·50	0·88	1·15	1·50	2·25
Titre (ml.)	4·01	3·60	3·05	2·65	2·30	1·56
Time (mins.)	0	0·44	0·81	1·20	1·96	2·71
Titre (ml.)	3·90	3·51	3·00	2·51	1·77	1·28

The % change–time curve from these two sets of measurements gave the following series of bimolecular coefficients :

x	10	20	30	40	50	60
k_2	20	27	33	40	46	53

As the time intercepts for different initial concentrations indicated a bimolecular reaction, the rising values of k_2 suggest that the reaction is autocatalytic. With *m*-NO_2·C_6H_4·CH:CH·COPh, under similar conditions, the autocatalysis becomes relatively less :

x	10	20	30	40	50	60
k_2	37	42	48	54	61	65

It is possible that the autocatalysis is due to hydrobromic acid produced by a concomitant electrophilic bromination, which would be less for the nitro-compound. Tests at the end of such reactions by adding silver nitrate dissolved in warm acetic acid showed a faint turbidity, indicating a small formation of hydrobromic acid, but possibly sufficient to cause the effect observed, as hydrobromic acid is a strong catalyst of the reaction. A rate comparison for these two compounds under conditions where acid autocatalysis is largely eliminated, namely, reactants M/320, HBr M/320, in CCl_4, 16°, showed Ph·CH:CH·COPh, $k_2 = 7{\cdot}3$, and *m*-NO_2·C_6H_4·CH:CH·COPh, $k_2 = 6{\cdot}7$. This result confirms the conclusion previously reached that, for nucleophilic bromine addition to the benzylideneacetophenones, there is relatively little change in rate from compound to compound.

The bimolecular coefficients quoted in the text are for the rapid reactions at $x = 50\%$ bromine or chlorine absorption, for the slow reactions at $x = 10\%$, whilst in the very slow reactions, where the change was of the same order as the experimental error, the results are given as $k_2 < 0{\cdot}0005$. The measurements with the quinones were less well reproducible than with the ketones, as a back reaction with the dibromo-product and potassium iodide tended to make the end-point uncertain. The times for the measurements in 1% aqueous acetic acid, from which the relative rates in the last table were derived, were for $x = 50$, benzoquinone, $t = 1{\cdot}7$, $2{\cdot}2$; naphthaquinone, $t = 4{\cdot}5$, $4{\cdot}8$; xyloquinone, $t = 65$, 65.

Victoria University College, Wellington, New Zealand. [*Received, July 5th*, 1947.]