

*The Influence of Alkyl Groups upon Reaction Velocities in Solution  
Part VI.\* The Acid-catalysed Prototropy of Dialkyl Ketones.*

By D. P. EVANS and J. R. YOUNG.

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The bromination of certain dialkyl ketones has provided results which, coupled with those of the previous papers, support Baker's views (*J.*, 1939, 1150) concerning the hyperconjugation of alkyl groups during prototropy as an explanation of changes in activation energy. Moreover, the changes of the *PZ* factor of the kinetic equation  $k = PZ \cdot e^{-E_a/RT}$ , may also be interpreted on the basis of hyperconjugation.

THE observations recorded in Part V\* have shown that in the ketones R·CO·R' conjugation in R affects the extent of hyperconjugative electron release from the alkyl groups R'. In order to apply these conclusions to the problem of the possible existence of hydrogen bonding in propiophenone and higher alkyl phenyl ketones (Parts I and II, *J.*, 1936, 785; 1938, 1434; cf. Baker, *J.*, 1939, 1150) the rates of acid-catalysed bromination of certain dialkyl ketones have been measured in 75% acetic acid. The results are given in the following Table, in which the values of *k* represent the fall in bromine titre in ml. of N/50-thiosulphate per min. for 20 ml. of 0.1M-ketone solution. Together with the results in Part I (*loc. cit.*), these results lead to the following conclusions.

Ketone	$k_{15}$	$k_{25}$	$k_{35}$	$k_{45}$	$k_{55}$	<i>E</i> (kcal.)	log <sub>10</sub> <i>PZ</i>
Me, Me .....	0.196	0.633	0.0272 (0°)	—	—	20.1	11.0
Et, Et .....	0.186	0.650	2.07	—	—	21.2	11.8
Pr <sup>i</sup> , Pr <sup>i</sup> .....	—	—	0.243	0.799	2.39	22.8	12.1
Pr <sup>n</sup> , Pr <sup>n</sup> .....	0.163	0.530	1.70	—	—	20.6	11.5
Bu <sup>t</sup> , Me .....	—	0.281	0.889	2.42	—	20.3	10.9
Bu <sup>t</sup> , Et .....	—	0.108	0.359	1.12	—	21.8	11.5
Bu <sup>t</sup> , Pr <sup>i</sup> * .....	—	—	0.0209	0.0718	0.207	22.7	11.1
Bu <sup>t</sup> , Pr <sup>n</sup> .....	—	0.096	0.308	0.096	—	21.3	11.1

\* The results for this ketone are less satisfactory than the others (see p. 1316) but are sufficiently accurate for comparison.

*Changes in Activation Energy.*—(1) (a) The trends of the values of *k* and of *E<sub>a</sub>* for the alkyl *tert.*-butyl ketones are similar to those found in Part I for the alkyl phenyl ketones. (b) The activation energy for *tert.*-butyl methyl ketone is only very slightly higher than that for acetone, which is identical with that for acetophenone. (c) The activation energy for *tert.*-butyl *isopropyl* ketone is measurably higher than any of the other values for the *tert.*-butyl series.

(2) In the dialkyl ketones, COR<sub>2</sub>, the energy of activation for diethyl ketone is higher than that for acetone, and the value of *E<sub>a</sub>* for di-*n*-propyl ketone approaches that of acetone. Finally, diisopropyl ketone exhibits a high *E<sub>a</sub>* value equal to that of *tert.*-butyl *isopropyl* ketone.

Observation 1(a) is not unexpected owing to the similarity in the variable alkyl groups in both series, but in the light of the wide difference in values between the dissociation constants of the cyanohydrins of corresponding members for the phenyl and the *tert.*-butyl alkyl ketones, the similarity of the actual *E<sub>a</sub>* values is surprising. We believe with Baker (*loc. cit.*) that the occurrence of a negative value of Δ*E<sub>a</sub>*(Me — Et) in both the phenyl and the *tert.*-butyl series, together with the approximate equality of the activation energies for the methyl members and for acetone [observation 1(b)], results from a compensation of

\* Part V, preceding paper.

hyperconjugation and inductive effects. This view also leads to a reasonable explanation of the changes in activation energies for the other dialkyl ketones.

Observation 1(c) is reminiscent of that found for the *isopropyl* group in combination with *tert.*-butyl in the cyanohydrin equilibria, where the very high dissociation constant of this ketone was explained on the basis of a steric (meshing) effect. A similar steric effect may operate in enolisation and hinder the approach of the proton to the ketone. With reference to observation 2, it is likely that a compensation of hyperconjugation and inductive electron release occurs which, coupled with steric effects in the branched-chain compounds, leads to the values of  $E_a$  observed.

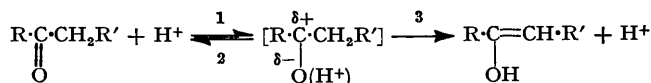
*Changes in the Factor log PZ.*—The variations in  $\log PZ$  for the dialkyl ketones are not large, but appear to be of sufficient magnitude and regularity to warrant interpretation on the basis suggested in Part I, *viz.*, that changes in  $PZ$  of the equation  $k = PZe^{-E_a/RT}$  may be due to the electron accession to carbonyl carbon affecting the proportion of activated complexes which form enol. The significant values of  $\log_{10} PZ$  from the present work and from Part I are listed below. In each case replacement of  $R' = \text{Me}$  by Et raises

Ketone R·CO·R'				Ketone R·CO·R'			
R	R'	$\log_{10} PZ$	$\Delta \log_{10} PZ$	R	R'	$\log_{10} PZ$	$\Delta \log_{10} PZ$
Ph	Me	10.7	+1.1	Bu <sup>t</sup>	Me	10.9	+0.6
Ph	Et	11.8		Bu <sup>t</sup>	Et	11.5	
Ph	Pr <sup>n</sup>	11.4	-0.4	Bu <sup>t</sup>	Pr <sup>n</sup>	11.1	-0.4
Ph	Pr <sup>i</sup>	11.1		Bu <sup>t</sup>	Pr <sup>i</sup>	11.1	
Me	Me	11.0	+0.8				
Et	Et	11.8					
Pr <sup>n</sup>	Pr <sup>n</sup>	11.5	-0.3				
Pr <sup>i</sup>	Pr <sup>i</sup>	12.1					

$\log PZ$ , the change being greatest in the phenyl compounds, less so in the methyl and ethyl compounds, and still less so in the *tert.*-butyl ketones. Further substitution of an additional methyl group to form the *n*-propyl ketones causes a fall in  $PZ$  in each case, and to a value intermediate between those for the corresponding methyl and ethyl compounds. Again, when the ethyl groups in the phenyl and *tert.*-butyl ethyl ketones are changed to *isopropyl* the values of  $PZ$  fall, but the value of  $PZ$  for the *disopropyl* ketones is the highest of all the compounds studied. This similarity in trends and the regularity of the variations in  $PZ$  in these series support the view that the changes are real and justify an interpretation.

The increases in  $PZ$  on passing (a) from acetone to diethyl ketone and (b) from methyl to ethyl *tert.*-butyl ketone are comparable with the change observed by Evans (*J.*, 1936, 785) in changing from acetophenone to propiophenone. We are now of the opinion that the explanation put forward in Part I (*loc. cit.*) for the changes in  $PZ$  in the prototropy of the alkyl phenyl ketones is not correct, for it involves only the inductive effect of alkyl groups attached to the  $\alpha$ -carbon atom.

Cardwell and Kilner (*J.*, 1951, 2431) reinvestigated and extended the earlier work of Catch, Elliott, Hey, and Jones (*J.*, 1948, 272) and Catch, Hey, Jones, and Wilson (*J.*, 1948, 276) on the ratio of the monobromination products of certain alkyl methyl ketones. They interpret the results on the basis of alkyl-group hyperconjugation with the developing double bond of the corresponding enol form. We are in full agreement with Cardwell and Kilner's conclusions on this point but wish to emphasize that the explanation provides strong corroborative evidence for the accuracy of the acid-catalysed enolisation mechanism proposed by Watson, Nathan, and Laurie (*J. Chem. Phys.*, 1935, 3, 170), *viz.*,



in which the rate of bromination is influenced by the proportion of transition complexes which form enol (stage 3) rather than reverting to ketone.

The changes in  $PZ$  for the prototropy experiments can readily be interpreted on this principle. Thus it is observed that substitution of a hydrogen atom in the methyl group

of R·CO·Me by a methyl group introduces hyperconjugative electron release to the  $\alpha$ -carbon atom during the formation of enol, with a consequent increase in the proportion of active complexes which form enol, and thereby enables us to account for the experimental increase in *PZ* for every R studied. The ionisation of the  $\alpha$ -hydrogen atom, although probably affected by the inductive effect of  $\alpha$ -methyl, is not influenced by the electromeric effects of the hyperconjugated hydrogen atoms, and in the formation of enol the hyperconjugation predominates over the inductive effect.

The case of diisopropyl ketone deserves special mention since here we have a symmetrical structure, and bromination in either group gives the same product. This, together with the hyperconjugation of six  $\beta$ -hydrogen atoms and the inductive effect of the  $\alpha$ -methyl groups, gives a proportion of enol which is higher than in any of the other ketones studied.

The results and conclusions of this and the preceding paper clearly indicate that the hydrogen-bond hypothesis advanced in Part I of this series is incorrect.

#### EXPERIMENTAL

*Materials.*—The ketones were prepared as described in Part V (preceding paper).

*Velocity Determinations.*—The results for acetone quoted in the Table on p. 1314 were taken from Bonner, Evans, and Watson (*J.*, 1939, 1353).

The brominations were carried out in 75% acetic acid containing 0.5M-hydrochloric acid; the medium was prepared, and the experiments were conducted, in the manner described by Evans, Morgan, and Watson (*J.*, 1935, 1167) and by Evans (Part I, *loc. cit.*); a similar accuracy of  $\pm 1.5\%$  was obtained in all cases but one. A typical set of results is given below.

#### *Bromination of tert.-butyl n-propyl ketone at 35°.*

Time (min.)	0	7	14	21	
Titre, ml. of N/50-Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> per 10 ml. ....	4.75	3.68	2.59	1.57	
Fall in titre per 10 ml. ....	—	1.07	2.16	3.18	
<i>k</i> <sub>35</sub> (fall in titre per 20 ml. per min.) .....	—	0.306	0.309	0.303	Mean 0.306

With *tert.-butyl isopropyl ketone* there was a tendency for the value of *k* to fall during the course of the experiment. This was not prevented either by repurification of the ketone or by slight changes in technique. The variation was similar at all temperatures, and so the value of *E<sub>a</sub>* for this ketone is less accurate than the others.

GLAMORGAN TECHNICAL COLLEGE, TREForest.  
WEST HAM COLLEGE OF TECHNOLOGY, LONDON, E.15.

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