252. *The Polar Effects of Alkyl Groups.*

By John W. Baker.

The values of the dipole moments of toluene, ethyl-, *iso*propyl-, and *tert.*-butyl-benzene (preceding paper) are interpreted on the basis of an inductive electron-release effect ($+I$) for alkyl groups increasing in the order $Me < Et < Pr^\beta < Bu^\gamma$, on which is superimposed a mesomeric electron-release ($+M$) of the Baker–Nathan type (J., 1935, 1844) which decreases in the order $Me > Et > Pr^\beta > Bu^\gamma$ but is of minor importance in the ground state of the molecule. In the transition state, in reactions which require electron-accession, the Baker–Nathan effect may be greatly enhanced ($+E$) and so assume the dominating rôle.

Using the correlation between the electron-release effects of substituent groups and energy levels contemporaneously being put forward by Hughes, Ingold, Masterman, and MacNulty, it is shown that the results of Baker, Nathan, and Shoppee for the effect of alkyl groups on the prototropic mobility of the methyleneazomethine system (J., 1935, 1847) and those of Evans on the acid-catalysed prototropy of the ketones $CH_2R{\cdot}COPh$ (J., 1936, 785) may be adequately explained on the basis of the combined polarisation and polarisability effects of alkyl substituents in the ground and transition states.

Much attention has recently been focused on the relative electron-release capacities of alkyl groups. Baker and Nathan (J., 1935, 1844) provided the first experimental evidence that the order of increasing electron-release $H < Me < Et < Pr^\beta < Bu^\gamma$ based on the general inductive effect ($+I$) is sometimes upset. The extreme velocity differences in the series of *p*-alkylbenzyl bromides were small but their relative magnitudes indicated a total electron-release decreasing in the order $\{Me > Et > Pr^\beta \approx Bu^\gamma\} > H$ for a reaction which requires electron-accession towards the side chain (Ingold and Rothstein's Class A). The difference between Pr^β and Bu^γ was within the experimental error but the main trend suggested a complete inversion of the general inductive order amongst the individual alkyl groups combined with retention of the theoretical position of the series as a whole relative to hydrogen.

In explanation of their kinetic results Baker and Nathan (*loc. cit.*) suggested an extension of the modern theory of resonance by assuming that the shared electrons of the H–C bond, attached to a suitably conjugated system, could also be involved in a resonance hybrid thus $H\text{—}\overset{\curvearrowright}{C}\text{—}\overset{\curvearrowright}{C{=}C}\text{—}\overset{\curvearrowright}{C{=}C}\text{—}$, the electron distribution of such a grouping being that which would result from resonance between structures of the types $H\cdot C\cdot C{:}C\cdot C{:}C\cdot$ (I) and $\overset{+}{H}\ C{:}C\cdot C{:}C\cdot \overset{-}{C}\cdot$ (II). Since each of the H–C bonds of the saturated carbon could thus function, this assumption provides a mechanism of electron-release (of the tautomeric type) which would decrease in the order Me > Et > Pr^{β} > Bu^{γ}.

Subsequently a considerable volume of evidence has been accumulated showing a partly inverted order for some members of the series. The significance of this evidence is discussed (and references are cited) in a parallel communication about to be published by Hughes, Ingold, and Taher, who have now obtained decisive evidence for the existence of the Baker–Nathan effect in a Class A reaction for which theory predicts its dominating importance.*

Baker, Nathan, and Shoppee (J., 1935, 1847) have also shown that the inverted order of electron-release is maintained by three of the groups in the series, *viz.*, Me > Pr^{β} > Bu^{γ}, in the retardation of a Class B reaction, *i.e.*, in one which is uniformly facilitated by electron-recession from the reacting centre. The incomplete character of this evidence demands caution in making theoretical deductions (cf. Hughes, Ingold, and Taher, *loc. cit.*), but it is a pointer to the inclusion of a permanent, mesomeric component (polarisation effect) in the electron-release mechanism suggested by Baker and Nathan. It was recognised (Baker, J., 1937, 1775) that the importance of the dipolar type (II) in the resonance hybrid, probably large in any appropriate reaction, might yet be small in the ground state of the molecule. The results now obtained for the dipole moments of the alkylbenzenes in the vapour phase (preceding paper) substantiate this view and permit a more comprehensive discussion of the whole problem in the light of recently accumulated evidence.

The observed zero moments for all the *cyclo*hexanes, combined with the known absence of a dipole moment in benzene itself, show that the moments of the corresponding alkylbenzenes must arise from electron displacement in the aromatic electronic system stimulated by the polar effect of the alkyl substituent. These moments fall into a regular series the order of which is that anticipated from the general inductive effects of alkyl groups. This result confirms the anticipation that the Baker–Nathan effect is unable to annul the usual inductive-effect order in the ground state of the alkylbenzene molecule, but the experimentally observed sequence for the values of μ is quite consistent with the simultaneous operation of both electron release mechanisms. This is illustrated in Fig. 1, where values, purely arbitrary in magnitude but in the correct relative order, are assigned to the electron-release by the inductive (Bu^{γ} > Pr^{β} > Et > Me) and the Baker–Nathan mechanism (Me > Et > Pr^{β} > Bu^{γ}), respectively, in units such that the numerical value of the *total* electron-release is $\mu \times 10^2$. Since the electron-release by the Baker–Nathan mechanism is dependent on the number of H–C linkings which are conjugated with the aromatic nucleus, the relative magnitudes of this effect have been denoted by 30, 20, 10, and 0 for Me, Et, Pr^{β} and Bu^{γ}, respectively. With the arbitrarily assigned values for the corresponding inductive effects (7, 38, 55, 70), the total electron-release (37, 58, 65, 70) follows the sequence which is experimentally observed.

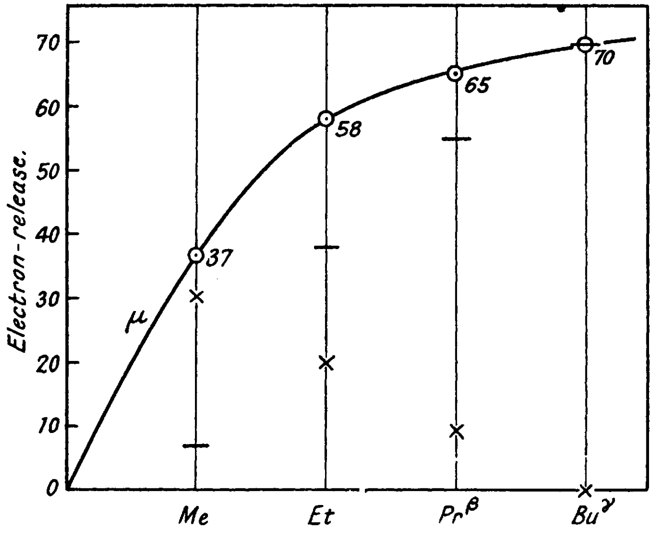
The clear-cut evidence now obtained by Hughes, Ingold, and Taher (*loc. cit.*) confirms the indication given by the almost completely inverted velocity order $\{Bu^{\gamma} \approx Pr^{\beta} < Et < Me\} > H$ observed by Baker and Nathan (*loc. cit.*) that, for Class A reactions, electron-release by the Baker–Nathan mechanism may sometimes assume the dominating rôle. In this respect it closely resembles the tautomeric (+ *T*) effect of the halogens (cf., *inter alia*, Ingold and Shaw, J., 1927, 2918; Baker, J., 1936, 1448; Bird and Ingold, J., 1938,

* The author is greatly indebted to Professor C. K. Ingold for private advance information of these results and of the theory correlating electron-release with energy levels (p. 1152) which has made possible this more comprehensive discussion of the significance of the dipole-moment data obtained by Baker and Groves.

918) where the incursion of polarisability effects (+ *E*) in reaction may upset the uniform order observed when only polarisation effects (— *I*, + *M*) are operative.

This view of the polar effects of alkyl groups readily accommodates most of the available experimental data, but the results obtained for the effects of *p*-alkyl substituents on the prototropic mobility of the methyleneazomethine system (Baker, Nathan, and Shoppee, *loc. cit.*) require a more detailed explanation. The essential feature of this reaction is that it is uniformly facilitated by electron-recession from the triad system and, conversely, is retarded by electron-accession towards this system. It must be emphasised that this conclusion is based upon the *experimentally* determined effects on velocity of *p*-substituents such as NMe_2 (retardation) and NO_2 or halogen (facilitation). It is thus in no way invalidated by Hsü, Ingold, and Wilson's proof (J., 1935, 1778) that the prototropic change proceeds by a termolecular mechanism involving the tautomeric molecule, an ethoxide ion, and a molecule of alcohol: the mesomeric ion $C_6H_4R\cdot\overset{\frown}{CH}\!\!-\!N\overset{\frown}{-}CHPh$, the formation of which by ionisation of the mobile hydrogen was assumed by Shoppee (J., 1933, 1117) to be the rate-determining stage, is never kinetically free.

FIG. 1.



Magnitude of electron-release in the ground state (arbitrary units).

— = +*I Effect.*
× = *Baker–Nathan effect.*
⊙ = *Total electron-release* ∝ *μ.*

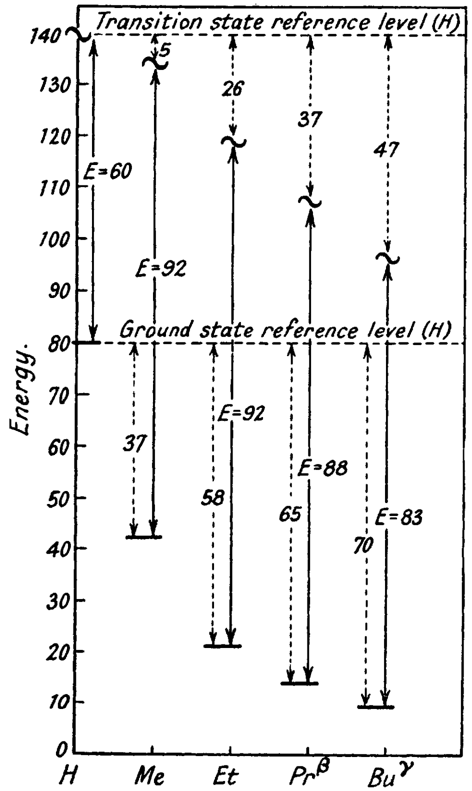
It was found that the retardation of this reaction by *p*-alkyl substituents was in the order Me > Pr^β > Bu^γ: the results are summarised in the following table.

R =	NMe₂.	Me.	Et.	Prβ.	Buγ.	OMe.	Cl.
$k_1 + k_2$ (hrs.$^{-1}$)	0·054	0·322	—	0·47	0·60	0·557	7·83
$\mu \times 10^{-18}$ of PhR (e.s.u.)	+ 1·39	0·37	0·58	0·65	0·70	— 0·80	— 1·56

It will be noticed that Shoppee's conclusion, that the values of $k_1 + k_2$ run parallel to the dipole moments of the compounds PhR, is not valid for the individual alkyl substituents within the group as a whole, but an electron-release, decreasing in the order Me > Pr^β > Bu^γ, is experimentally indicated. Assuming, as is now generally accepted, that the polar character of groups affects mainly the energy of activation *E* of a reaction, this implies a series of activation energies $E_H \lll E_{Me} > E_{Pr^\beta} > E_{Bu^\gamma}$.

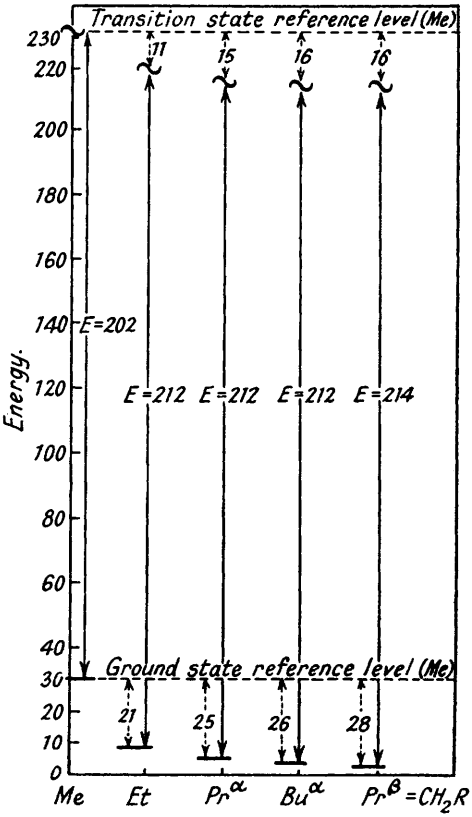
Explanation of these results is made possible by the application of a theory contemporaneously being put forward by Hughes, Ingold, Masterman, and MacNulty (private communication from Professor C. K. Ingold; cf., Ingold, *Nature*, 1938, **141**, 314) which correlates the relative magnitudes of electron-release with the relative energy levels in the molecule. These have already been discussed for the ground state of an alkyl-substituted benzene nucleus, but in evaluating the energies of activation the electronic energy levels in the transition state must also be considered. Since the reaction is one which requires electron-recession from the side chain to the nucleus, it is probable that, in the transition state, electron-accession by the Baker–Nathan mechanism (+ *T*) will be so greatly reduced as to become almost negligible. The energy levels will be determined essentially by an inductive effect, possibly also diminished, but to a smaller extent. An attempt is made to illustrate this in Fig. 2, where energy is plotted as ordinates. For simplicity it is

FIG. 2.



Relative energy levels (prototropy of azomethines):
— in ground state.
∼ in transition state.

FIG. 3.



Relative energy levels (acid-catalysed prototropy of ketones, $CH_2R\cdot COPh$*):*
— in ground state. ∼ in transition state.

assumed that, in the transition state, the Baker–Nathan mechanism is negligible and that the inductive effect of the alkyl substituents has been reduced to two-thirds of the arbitrary value assigned to it in the ground state.* The units, purely arbitrary and illustrative, are numerically the same as those employed in Fig. 1. On this basis the energy levels relative to those in the unsubstituted compound are denoted by the symbols — and ∼ in the ground and transition states, respectively. The differences in the heights of these two ordinates thus represent, in the arbitrary units, the values of the energies of activation for the reaction in the case of each alkyl substituent. The order is $E_{H} \ll (E_{Me} \sim E_{Et}) > E_{Pr\beta} > E_{Bu\gamma}$, in harmony with the experimentally observed velocity order $(v_{H} \gg) v_{Me} < v_{Pr\beta} < v_{Bu\gamma}$ $(v = k_1 + k_2)$.

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* The argument is in no way invalidated if the magnitude of the inductive effect is undiminished in the transition state.

This explanation illustrates the general method of approach to such problems. One further example of its application may be quoted. In the acid-catalysed prototropy of phenyl alkyl ketones, $CH_2R{\cdot}COPh$, Evans (J., 1936, 785) obtained the following values for *E* :

R =	H.	Me.	Et.	Pr^a.	(Pr$^\beta$ = CH_2R).
E (kg.-cals./mol.)	20·2	22·1	22·0	21·7	22·1

The sudden and large increase in passing from acetophenone to propiophenone, and the identical values observed for propiophenone and *iso*butyrophenone were unexpected by Evans and called forth a special explanation involving the co-ordination of a β-hydrogen atom with the unshared electrons of the oxygen of the carbonyl group. The results may be adequately explained on the basis of the combined polarisation and polarisability effects of the alkyl group CH_2R.

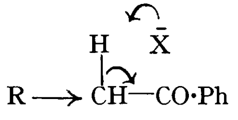
The reaction is one which experimental data, independently of any theory of mechanism, prove to be facilitated by electron-release towards the carbonyl group. In this case the reference standard is the electron-release capacity of the methyl group (R = H) in acetophenone and, in Fig. 3, the ordinates which represent energy levels in the ground (—) and activated (~) states of this compound are arbitrarily chosen so that their difference (*E*) is 202. The arbitrary values assigned to the electron-release by the group CH_2R as a whole are summarised in the following table, and the *differences* between these values and the value for CH_3 are denoted in Fig. 3.

	Ground state.				Activated state.			
Group CH_2R.	+ *I*.	+ *T*.	Total.	Diff.	+ *I*.	+ *T*.	Total.	Diff.
Me	7	30	37	—	7	45	52	—
Et	38	20	58	21	38	25	63	11
Pr^a	42	20	62	25	42	25	67	15
Bu^a	43	20	63	26	43	25	68	16
Pr$^\beta$	55	10	65	28	55	13	68	16

The values assigned in the ground state are those used in the prototropy of the azomethine system, those for the + *I* effect of Pr^a and Bu^a being slightly higher than that of Et. In the transition state, since the reaction requires electron-accession, it is to be anticipated that the value of the + *E* effect will be enhanced. Since the α-hydrogen atoms participating in this effect are those the ionisation of which is the reaction under examination, a statistical factor is involved arising from the presence of three α-hydrogen atoms in CH_3, two in Et, Pr^a, and Bu^a, and only one in Pr$^\beta$, and weight has been assigned to this factor in assessing the increases involved.

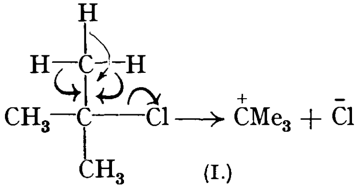
Examination of Fig. 3 shows that, in the arbitrary units employed, the values of *E* for CH_2R = Me, Et, Pr^a, Bu^a, and Pr$^\beta$ are 202 (standard), 212, 212, 212, 214, respectively. These are qualitatively in harmony with the experimental results, *viz.*, a large increase in *E* occurs in passing from acetophenone to propiophenone and the values for the latter ketone and for *iso*butyrophenone are approximately equal. It is thus evident that, given suitable magnitudes for the polarisation and polarisability factors which are in qualitative agreement with theory and general experience, the results *can* be explained without the introduction of the *ad hoc* theory advocated by Evans.

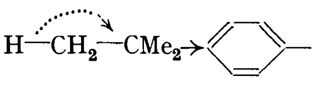
In the base-catalysed prototropy of the ketones, the present author prefers a mechanism based on the more usual direct attack of the basic catalyst at the ionising hydrogen. If this is so then the carbonyl group is only indirectly involved and the main effect of the group R will thus be its inductive electron-release towards the α-carbon atom (see inset). Increase in the + *I* effect of R would cause a small and continuous increase in the value of *E*, a conclusion which is also substantiated by the experimental observations.



The Baker–Nathan effect is thus of the same type as the classical tautomeric effect (+ *T*) except that, in the latter case, it arises from the participation of an *unshared* electron pair (or the π electrons of a multiple link) in a conjugated system. It may thus be denoted by the same symbols. Like the tautomeric effect it consists of a permanent, mesomeric component (+ *M*) operative in the ground state of the molecule, and an electromeric portion (+ *E*) the magnitude of which depends on the electronic requirements of the transition state in reaction.

In assessing the importance of this + *T* effect, it must again be stressed that the presence of the necessary conjugated system is of fundamental importance. Such a system may either be the more formal type with alternate single and multiple linkings or it may be completed by a group which, in the reaction, separates with its bonding electrons. It is, for example, important (with respect to nine H–C linkings) in the reactions of *tert.*-butyl halides with nucleophilic reagents which require the separation of halide ion (I), but not in the corresponding *p*-*tert.*-butylphenyl derivatives (II). It would not be operative in, for example, the thermal decomposition of quaternary phosphonium hydroxides (III) (Fenton and Ingold, J., 1929, 2342; Hey and Ingold, *ibid.*, 1933, 531), in the acid and the alkaline hydrolyses of alkyl esters, (IV) and (V) respectively (Ingold and Ingold, J., 1932, 756), or in the fission of mercury dialkyls with hydrochloric acid (VI) (Kharasch and Flenner, *J. Amer. Chem. Soc.*, 1932, **54**, 674). In all these reactions the normal order of inductive electron-release, Me < higher alkyl, is observed, and it is the absence of the system necessary for the operation of the Baker–Nathan effect which, in the author's opinion, determines this result, not the fact that the alkyl group is directly involved in the reaction (Ayling, J., 1938, 1014).


(I.)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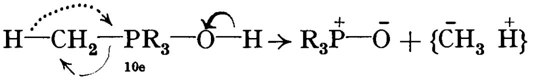
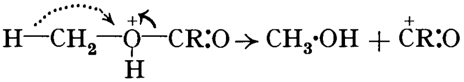
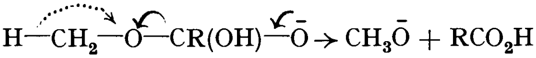
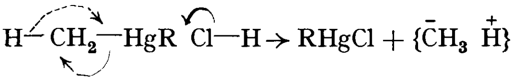

$\mathrm{H{-}CH_2{-}PR_3{-}O{-}H \rightarrow R_3\overset{+}{P}{-}\overset{-}{O} + \{\overset{-}{C}H_3\ \overset{+}{H}\}}$ (III.)


$\mathrm{H{-}CH_2{-}\overset{+}{O}(H){-}CR{:}O \rightarrow CH_3{\cdot}OH + \overset{+}{C}R{:}O}$ (IV.)


$\mathrm{H{-}CH_2{-}O{-}CR(OH){-}\overset{-}{O} \rightarrow CH_3\overset{-}{O} + RCO_2H}$ (V.)


$\mathrm{H{-}CH_2{-}HgR\ Cl{-}H \rightarrow RHgCl + \{\overset{-}{C}H_3\ \overset{+}{H}\}}$ (VI.)

Summarising, the resultant polar effects of primary, secondary, and tertiary alkyl groups are regarded as being dependent jointly on the following factors:

(1) An inductive, and inductomeric, effect (+ *I*) increasing in the order Me < Et < Pr^{β} < Bu^{γ}.

(2) A tautomeric electron-release, decreasing in the order Me > Et > Pr^{β} > Bu^{γ}, of the type suggested by Baker and Nathan, which is of minor importance in the ground state of the molecule (+ *M*) and in reactions which require electron-recession from the reaction centre, but which may assume the major rôle in reactions which require electron release (+ *E*), always providing that the appropriate system be present.

(3) A purely steric (spatial) effect increasing in the order Me < Et < Pr^{β} < Bu^{γ} when the alkyl group is substituted directly at the seat of the reaction.

Discussion of the effect of alkyl groups conjugated with a carbonyl group is reserved until the completion of investigations, at present in hand, on the cyanohydrin reaction of *p*-alkylbenzaldehydes.

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