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# ROLE OF SOLVENT IN ALKYL SUBSTITUENT EFFECTS

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**Abstract**—From the energies of electronic transitions that place a high electron demand on alkyl substituents (e.g., the "principal" transition of *p*-alkylnitrobenzenes in the gas phase) it is concluded that the inherent order of electron release is: $Bu^t > Pr^i > Et > Me$. For $RCH_2$ groups larger spreads are found, in the release order: $Pe^{neo} > Bu^i > Pr > Et > Me$. A Baker–Nathan effect has been found in the principal electron-transition energies of *p*-alkylnitrobenzenes and *p*-alkylacetophenones in basic solvents. This effect is attributed to steric hindrance to solvation of the electron-deficient aromatic ring in the vicinity of the alkyl substituent.

In electronic transitions of the type in which a substituent is called upon strongly to accept negative charge (e.g., the "principal" transition of *p*-alkylphenols in the gas phase) it has been found that alkyl groups are apparently better electron *acceptors* than a hydrogen.

Rate constants and heats and entropies of activation obtained in the solvolysis of 3,5-dimethyl- and 3,5-di-*tert*.-butyl-benzhydryl chlorides are compared with corresponding results on mono *m*- and *p*-alkylbenzhydryl chlorides. The assumption that the Baker–Nathan effect in this system is due to a C–H hyperconjugative order of electron release by alkyl groups does not satisfactorily account for the results. On the other hand, the results are completely consistent with the viewpoint that the Baker–Nathan effect is due to steric hindrance to solvation of electron-deficient sites in the near vicinity of the alkyl substituent.

IT has been pointed out recently that the original theory of Baker and Nathan[1] is unable to embrace many facts apparently within its proper province, and three suggestions for modification or replacement of the theory appeared practically simultaneously.[2, 3, 4] Sweeney and Schubert have suggested that even in the face of a high electron demand, the inherent electron release by alkyl groups may still be in the inductive order. It was not concluded that C–H hyperconjugation is necessarily inoperative; only that, *if* it is operative, other release modes in the inductive order (i.e., the inductive effect and possibly C–C hyperconjugation) may still predominate when alkyl is attached to a highly electron-deficient unsaturated system.[5] An inversion in the order of experimental quantities such as rate and equilibrium constants; i.e., the Baker–Nathan effect is then ascribed to steric hindrance to solvation of electron-deficient sites in the near proximity of the alkyl group.[3] Earlier, Price and Lincoln had suggested that a bulky group such as $Bu^t$ may shield the direct reaction site from solvation.[6] Shiner has suggested that the role of the solvent is to enhance C–H over C–C hyperconjugation, by incipient hydrogen-bonding of the solvent with the $\alpha$ hydrogens of the alkyl substituent.[2] Burawoy and Spinner have chosen to neglect the role of the solvent, except possibly insofar as it may act to change the demand for electrons placed upon the alkyl group. They consider the Baker–Nathan effect to be caused by steric hindrance to bond shortening, with the alkyl groups releasing only by the inductive mechanism.[4]

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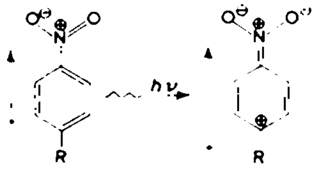
[1] J. W. Baker, *Hyperconjugation*. Oxford University Press (1952).
[2] V. J. Shiner, Jr., *J. Amer. Chem. Soc.* **76**, 1603 (1954).
[3] W. A. Sweeney and W. M. Schubert, *J. Amer. Chem. Soc.* **76**, 4625 (1954).
[4] A. Burawoy and E. Spinner, *J. Chem. Soc.* 3752 (1954).
[5] W. M. Schubert and W. A. Sweeney, *J. Org. Chem.* **21**, 119 (1956).
[6] C. C. Price and D. C. Lincoln, *J. Amer. Chem. Soc.* **73**, 5836 (1951).

Contradiction to the original theory is found mainly in the energies of transitions of the type in which the Franck–Condon principle applies, i.e., electronic transitions.[5] A specific example is seen in the data of Table 1, which gives the energies the so called principal band transition of *p*-alkylnitrobenzenes and *p*-alkylacetophenones *in the gas phase*. The principal band (also called *K*-band) has been identified as due to a dipolar transition in the long axis of the molecule. It is approximately described by the valence-bond structures (I) and (II), which are representative of the ground and excited states, respectively.[7]



(I) (II)

TABLE 1. VALUES OF $\nu_R - \nu_{Me}$ ($cm^{-1} \pm 30\ cm^{-1}$) FOR THE PRINCIPAL BAND OF *p*-ALKYLNITROBENZENES AND *p*-ALKYLACETOPHENONES IN THE GAS PHASE[8, 9]

| R= | H | Me | Et | Pr$^i$ | Bu$^t$ |
|---|---|---|---|---|---|
| *p*-$RC_6H_4NO_2$ | +1850 | 0* | −130 | −180 | −210 |
| *p*-$RC_6H_4COCH_3$ | +1370 | 0† | −110 | 140 | −160 |
| *p*-$RCH_2C_6H_4NO_2$ | 0* | −130 | −220 | 370 | −480 |

* Nitrotoluene has $\nu_{max} = 39970\ cm^{-1}$.
† *p*-Methylacetophenone has $\nu_{max} = 41860\ cm^{-1}$.

For the series R, rows 1 and 2 of Table 1, it is seen that the stabilization of the highly electron-demanding excited state relative to the ground state takes the order: Bu$^t$ > Et > Me ≫ H.[8] The excitation energy of the *iso*propyl compound of either series lies between those of the corresponding *tert.*-butyl and ethyl compounds, but is within experimental error of the *tert.*-butyl compound in the nitrobenzene series and of both the ethyl and *tert.*-butyl compounds in the acetophenone series. It is concluded from these gas-phase results that the *inherent* order or electron release is the inductive one, at least in these electronic transitions. The order of electron release in the series $RCH_2$, row 3 of Table 1, is: Pe$^{neo}$ > Bu$^t$ > Pr > Et > Me.[9] Furthermore, *neo*pentyl is inherently a more efficient electron-releasing group than either methyl or *tert.*-butyl. Therefore, steric inhibition of hyperconjugation[10, 11, 12] is not important in the electron-release effects of the alkyl groups, at least for these systems.*

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* The "extra" activating effect of the *neo*pentyl group and the relatively large spreads in excitation energy for the series $RCH_2$ may mean that, in addition to a polarization through the bond to the substituent, there is a direct polarization across space by the electron-deficient ring of that portion of the alkyl group that closely overhangs the ring.[9]

[7] W. T. Simpson and A. G. Albrecht, *J. Amer. Chem. Soc.* **77**, 4455 (1957), and preceding papers.
[8] W. M. Schubert, J. Robins and J. L. Haun, *J. Amer. Chem. Soc.* **79**, 910 (1957).
[9] W. M. Schubert and J. Robins, *J. Amer. Chem. Soc.* **80**, 559 (1958).
[10] V. H. Shiner, Jr., *J. Amer. Chem. Soc.* **78**, 2654 (1956).
[11] R. T. Arnold and W. L. Truett, *J. Amer. Chem. Soc.* **73**, 5508 (1951).
[12] G. Baddeley and M. Gordon, *J. Chem. Soc.* 2191 (1952).

The effect of a wide variety of solvents on the principal band transition energy of both R series of Table 1 and of *p-neo*pentylnitrobenzene has been determined.[8, 9] The important result is that the Baker–Nathan effect was observed in basic solvents. That is, for the R series of both the nitrobenzenes and acetophenones, basic solvents (water was the most effective) gave a jumbled order of excitation energies tending toward a complete Baker–Nathan order. The spread in excitation energy between *p-neo*pentyl- and *p*-methyl-nitrobenzene also was noticeably reduced in basic solvents (e.g., $\nu_{Me} - \nu_{Pe^{neo}} = 270\ cm^{-1}$ in *n*-butylamine). From these results, it was concluded that at least for these electron transitions, the Baker–Nathan effect is not caused by an inversion in the *inherent* inductive *order* of electron release but is due to an indirect solvent effect. Explanation of these results can be found in terms of steric hindrance to solvation of electron-deficient sites in the near vicinity of the alkyl group. Even though practically no movement of solvent molecules is allowed in the short time of the electronic transition (Franck–Condon principle), solvent stabilization by basic species at electron-deficient sites in the ring should be greater in the excited state than in the ground state of this particular transition.[8, 9] The bulkier the alkyl substituent, then, the greater would be interference with solvent stabilization of the excited state relative to the ground state, and hence the less would be the solvent lowering of the excitation energy.[*] An equally satisfactory qualitative explanation of these solvent effects can be found in terms of Shiner's idea of solvent enhancement of C–H hyperconjugation, provided it is assumed that there is steric hindrance to solvation of the α hydrogens of the *neo*pentyl group. However, steric hindrance to ring solvation appears to give a more satisfactory explanation of the results of a quantitative treatment of the solution data made in terms of a linear free-energy relationship.[7, 8] Thus there is found a very good linear proportionality between solvent effects for Me vs. H compounds, but a relatively poorer proportionality between solvent effects for $Bu^t$ vs. H and $Pe^{neo}$ vs. H.[8, 9]

In a search for possible direct evidence for solvent enhancement of C–H hyperconjugation, a comparison of the principal band excitation energies of *p*-trideuteromethyl- and *p*-methyl-nitrobenzene has been made. The results obtained are given in Table 2.

TABLE 2. EXCITATION ENERGY SPREADS ($\pm 15\ cm^{-1}$) FOR *p*-NITROTOLUENES

| | Heptane | $Bu^nNH_2$ | $Bu^tOH$ | Dioxan | 95% EtOH | $H_2O$ | 52% $HClO_4$ | 96% $H_2SO_4$ | 70% $HClO_4$ |
|---|---|---|---|---|---|---|---|---|---|
| $\nu_H - \nu_{CH_3}$ | 1810 | 1920 | 1960 | 2090 | 2090 | 2280 | 2480 | 2710 | 2750 |
| $\nu_{CD_3} - \nu_{CH_3}$ | 50 | 40 | 40 | 30 | 30 | 50 | 60 | 70 | 70 |

The $\nu_{CD_3} - \nu_{CH_3}$ spreads show no detectable tendency predictable on the basis of solvent enhancement of C–H hyperconjugation; i.e., the spreads are not markedly altered in basic solvents of the type most likely to be involved in incipient hydrogen bonding at the α hydrogens (deuteriums). The only discernible trend is a slight increase in $\nu_{CD_3} - \nu_{CH_3}$ in more acidic solvents. This indicates that the methyl group

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[*] The Baker–Nathan effect, although frequently observed in chemical transitions in solution, is rarely observed in electronic transitions in solution. This can be attributed to the fact that, owing to the Franck–Condon principle, the excited electronic states are not maximally solvated.

has a slightly larger absolute value of the Hammett $\sigma$ constant than the CD$_3$ group. In fact, a plot of $\nu_{CH_3} - \nu_H$ vs. $\nu_{CD_3} - \nu_H$ with changing solvent gives a line with a slope, $\sigma_{Me}/\sigma_{CD_3}$, of 1·036 ± 0·002 and a correlation coefficient of $r = 0·999$.

TABLE 3. VALUES OF $\nu_R - \nu_{Me}$ (cm$^{-1}$ ± 20 cm$^{-1}$) FOR THE PRINCIPAL BAND OF 4-ALKYLPYRIDINIUM IONS IN 1% HClO$_4$ AND 4-ALKYL-1-HYDROXYPYRIDINIUM IONS IN 9% HClO$_4$

| Series R, | R | H | Me | Et | Pr$^i$ | Bu$^t$ |
|---|---|---|---|---|---|---|
| 4-RC$_5$H$_4$NH$^+$ | | −3820 | 0* | 430 | 650 | −900 |
| 4-RC$_5$H$_4$NOH$^+$ | | −1680 | 0† | −250 | −350 | −480 |
| Series RCH$_2$, | R = | H | Me | Et | Pr$^i$ | Bu$^t$ |
| 4-RCH$_2$C$_5$H$_4$NH$^+$ | | 0* | 430 | 860 | – | 1910 |
| 4-RCH$_2$C$_5$H$_4$NOH$^+$ | | 0† | −250 | −510 | – | −1160 |

* 4-Methylpyridinium ion has $\nu_{max}$ = 46,080 cm$^{-1}$.
† 4-Methyl-1-hydroxypyridinium ion has $\nu_{max}$ = 44,000 cm$^{-1}$.

The effect of alkyl substitution upon the energy of the principal electronic transition of a number of positive ions in solution has been determined. The most complete series studied are the 4-alkylpyridinium ions and 4-alkyl-1-hydroxypyridinium ions. Excitation-energy data for the pyridinium ions in 1 per cent HClO$_4$ and the 1-hydroxypyridinium ions in 9 per cent HClO$_4$ are given in Table 3. Qualitatively, the effects of alkyl substitution in these solution spectra is the same as for nitrobenzene and acetophenone in the gas phase. That is, the series R follows the inductive order of excitation energies, and the same order of excitation energies is followed by the series RCH$_2$ as by the series R. The spreads in the excitation energy data of Table 3 are quite large. Note also that the larger H–Me spread for the pyridinium ions compared to the 1-hydroxypyridinium ions is associated with a larger spread among the alkyl compounds.* The effects of changing solvent also has been studied, although the types of solvents that can be used with these ions is somewhat limited. The solvent shifts are small and the same qualitative order of excitation energies was observed in all solvents used. The pyridinium ion spectra moved slightly to lower energies as solvent basicity was decreased, while the hydroxypyridinium ion spectra moved slightly to higher energies. An approximate balance between solvent stabilization of ground and excited states is indicated by the smallness of the solvent shifts. This is not surprising in view of the fact that the excitation involves a redistribution of positive charge (equation (2) is a crude valence bond representation of this transition); i.e., the decrease in solvent stabilization at sites decreasing in positivity on excitation is

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* Large wavelength spreads, in the inductive order, also are seen in the spectra of a number of *p*-alkyldi- and *p*-alkyltri-arylmethyl carbonium ions in concentrated sulfuric acid. For example, the principal band of di-(*p*-*tert*.-butylphenyl)methyl carbonium ion lies 8 mμ above that of the dimethyl homologue.[13] However, at the high wavelengths of these principal bands, the spread in frequency is only 350 cm$^{-1}$.

[13] N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Org. Chem.* **19**, 155 (1954); *J. Amer. Chem. Soc.* **77**, 3044 (1954).

(3)

approximately balanced by the increase in solvent stabilization at sites increasing in positivity. The fact that the solvent shifts are small indicates that the order of excitation energies observed here probably represents the inherent order of electron release by the alkyl substituents in these transitions. The same trends, with less complete series, are also found in the principal band spectra of the conjugate acids of *p*-alkylacetophenones in concentrated sulfuric acid solution and *p*-alkylnitrobenzenes in fuming sulfuric acid.

*Alkyl groups as acceptors of negative charge*

It was deemed of interest to determine the effect of alkyl substituents in an electronic transition in which the substituent is called upon strongly to accept electrons. Such a transition is the "principal" electronic transition of phenol, anisole, aniline and dimethylaniline, represented approximately by equation (3). Results for the *p*-hydrogen, *p*-methyl and *p-tert.*-butyl compounds in the gas phase at 100–150° are given in Table 4.

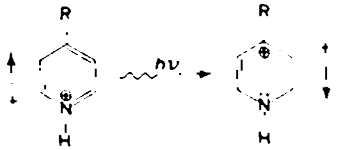

TABLE 4. VALUES OF $\lambda_{max}$ (mμ) FOR THE PRINCIPAL ELECTRONIC BAND OF PHENOLS, ANISOLES, ANILINES AND N N-DIMETHYLANILINES*

| | H | Me | $\mathrm{Bu}^t$ |
|---|---|---|---|
| Z = OH | 206·3 | 216·1 | 216·0 |
| Z = $OCH_3$ | 215·0 | 219·8 | 219·9 |
| Z = $NH_2$ | 229·4 | 233·7 | 232·7 |
| Z = $NMe_2$ | 241·8 | 243·5 | 244·5 |

* The band position is unchanged over a temperature range of 100–150°.

Somewhat surprisingly, it is seen that the excitation energies of the *para*-methyl and *para-tert.*-butyl compounds lie below those of the parent *para*-hydrogen compound in each case. No significance should be attached to the relative $\lambda_{max}$ values for the principal band of methyl and *tert.*-butyl compounds, since the principal bands are somewhat asymmetric, owing evidently to a near-lying lower wavelength transition. However, the principal band for each alkyl compound clearly lies at longer wavelengths than that of the corresponding hydrogen compound. In view of the nature of the transition, these results imply that alkyl groups are better electron *acceptors* than hydrogen when called upon strongly to accept electrons. This suggests that an alkyl group is more readily polarized than hydrogen when attached to a highly electronrich system as well as when attached to an electron-deficient system.[9, 14] In general, when an alkyl substituent is called upon to accept electrons in a chemical transition, it apparently does so less readily than hydrogen. Examples include the base catalyzed hydrolysis of ethyl *p*-alkylbenzoates[*] [15] and activated nucleophilic aromatic substitution.[16] It seems likely that the substituent is not called upon to accept negative charge as strongly as in the above-mentioned electronic transitions. It has been suggested that the ability of the substituent to accept negative charge is a function of both its electronegativity and its polarizability.[9, 14] Presumably hydrogen as a substituent is more electronegative than alkyl but less polarizable. In that event, it is possible that in the chemical transitions the qualitative order of electron acceptance is governed primarily by the electronegativity of the substituent, whereas in the electronic transitions it is governed primarily by the polarizability of the substituent.

### *The Baker–Nathan effect in chemical transitions*

It remains to be seen whether conclusions made about alkyl substituent effects in electronic transitions can be extrapolated to chemical transitions. The assumption made originally by Baker and Nathan, that alkyl groups release electrons in the C–H hyperconjugative order in the face of a high electron demand, is consistent primarily only with solution rate and equilibrium data.[5] However, if it is assumed that alkyl electron release is in the inductive order, whether the demand for electrons be low or high, the idea that steric hindrance to solvation of electron-deficient sites attached to the alkyl group acts to give the Baker–Nathan effect is consistent with a wide variety of both physical and chemical data on alkyl compounds.

TABLE 5. SOLVOLYSIS OF $p$-$RC_6H_4CHClC_6H_5$ IN "80%" ACETONE[17]

| R = | H | Me | Et | $Pr^i$ | $Bu^t$ |
|---|---|---|---|---|---|
| $k \times 10^6$ sec$^{-1}$ (0°) | 2·82 | 83·5 | 62·6 | 46·0 | 35·9 |
| $\Delta H^{\ddagger}$ | 20·5 | 18·3 | 18·9 | 19·3 | 19·5 |
| $\Delta S^{\ddagger}$ | 8·9 | −9·8 | 8·6 | −7·7 | −5·6 |

As a typical example of the kind of observation on which the theory of Baker and Nathan is based, consider the solvolysis of *p*-alkylbenzhydryl halides in "80%" acetone (Table 5). Both the rate constants and heats of activation show a Baker–Nathan effect. This is of course consistent with the conclusion that inherent release by the alkyl groups in this transition is in the C–H hyperconjugative order. However, rate constants, heats of activation *and* entropies of activation are consistent with the viewpoint that inherent release by alkyl is in the inductive order and steric hindrance to solvation acts to invert the rate order.[†] [5] In the *meta*-alkyl series in the same solvent

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[*] Rate constants for this reaction follow the inductive order in 56% acetone and the C–H hyperconjugative order in 85% ethanol.[15]

[†] Steric hindrance to solvation of electron-deficient sites in the substituted aromatic ring of the polar transition state would increase $\Delta H^{\ddagger}$ and this would act to decrease $k$. The same factor would increase $\Delta S^{\ddagger}$, by increasing the solvation entropy of the transition state, and this would tend to increase $k$. Presumably solvation effects on $\Delta H^{\ddagger}$ are more important in governing the $k$ values.

[14] W. M. Schubert, J. M. Craven, H. Steadly and J. Robins, *J. Org. Chem.* **22**, 1285 (1957).
[15] E. Berliner, M. C. Beckett, E. Blommers and B. Newman, *J. Amer. Chem. Soc.* **74**, 4940 (1952).
[16] E. Berliner and L. C. Monack, *J. Amer. Chem. Soc.* **74**, 1574 (1952).
[17] E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.* 950 (1940).

a mild Baker–Nathan effect on the rate constants is observed (Table 6). Similar results are found in the solvolyses of *m*-alkylphenyldimethylcarbinyl chlorides in "90%" acetone at 25°.[19] Despite the small methyl-hydrogen rate constant spread, Berliner and H. C. Brown have attributed this result to "*meta*" C–H hyperconjugation being important enough to tend to give a C–H hyperconjugative order of release by the alkyl groups. However, the rate results are equally consistent with the operation of mild steric hindrance to solvation of the substituted aromatic ring.* Unfortunately the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are so close that no significance can be attached to their differences. The fact that the Baker–Nathan effect in the rate constants is weaker for the *meta*-alkyl than for the *para*-alkyl compounds would be difficult to rationalize in terms of steric hindrance to solvation of the direct reaction site (i.e., the central carbon atom),[6] but is consistent with steric hindrance to solvation *near* the alkyl group. In other words, steric hindrance to solvation of the electron-deficient ring of the transition state would be expected to be less of a factor in the *meta*-alkyl series than in the *para*-alkyl series, since in the *meta*-alkyl compounds the substituent is further removed from the sites of greatest electron deficiency in the ring. It is interesting to note that whereas the *meta*-methyl and *tert*.-butyl rates have the C–H hyperconjugative order in "80%" acetone, they are in the inductive order in "90%" ethanol (Table 6).[19] This shows that the Baker–Nathan effect on rate constants is solvent dependent, as pointed out by Shiner, who found that the effect of changing solvent upon the rate constants of the *meta*-alkyl compounds can be rationalized either in terms of steric hindrance to solvation and/or solvent enhancement of C–H hyperconjugation.[19]

TABLE 6. SOLVOLYSIS OF *m*-$RC_6H_4CHClC_6H_5$

| R - | H | Me | Bu$^t$ |
|---|---|---|---|
| "80%" *acetone*[18] | | | |
| $k \times 10^4$ sec$^{-1}$ (0°)* | 2·79 | 4·78 | 4·27 |
| $\Delta H^{\ddagger}$ | 20·6 | 20·4 | 20·5 |
| $\Delta S^{\ddagger}$ | 8·9 | 8·3 | 8·2 |
| "90%" *ethanol*[20] | | | |
| $k \times 10^4$ sec$^{-1}$ (0°) | 20·5 | 39·6 | 47·0 |

* The rate constants for ethyl and *iso*propyl are 4·28 and 3·93, respectively.[18]

A study has been made of the solvolysis of *meta*-dimethyl- and *meta*-di-*tert*.-butylbenzhydryl chlorides in "80%" acetone and "90%" ethanol. The expectation, in terms of steric hindrance to solvation, is that the second *tert*.-butyl group would considerably increase solvent shielding of electron-deficient sites in the substituted ring. This should result in a reduced activating effect by the second *tert*.-butyl group and an increase in both the heat and entropy of activation in proceeding from the dimethyl

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* It is presumed that the positive charge in the substituted ring is distributed mainly to the *ortho* and *para* positions and that a bulky alkyl substituent in the *meta* position hinders ring solvation less than it does when attached to the *para* position.[5] Berliner and Chen have expressed a contrary opinion.[18]

[18] E. Berliner and M. M. Chen, *J. Amer. Chem. Soc.* **80**, 343 (1958).

[19] H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *J. Amer. Chem. Soc.* **79**, 1897 (1957).

[20] V. J. Shiner, Jr. and C. J. Verbanic, *J. Amer. Chem. Soc.* **79**, 371 (1957).

to the di-*tert.*-butyl compound. The results of Table 7 show that these expectations have been realized.

TABLE 7. SOLVOLYSES OF 3, 5-DIALKYLBENZHYDRYL CHLORIDES

| R = | H | Me | Bu$^t$ |
|---|---|---|---|
| "80%" *acetone*: | | | |
| $k \times 10^5$ sec$^{-1}$ (0°) | 0·279[18] | ·955 | ·729 |
| $k \times 10^5$ sec$^{-1}$ (35°) | · | 70·8 | 60·5 |
| $\Delta H^{\ddagger}$ | 20·6[18] | 20·0 | 20·5 |
| $\Delta S^{\ddagger}$ | 8·9[18] | 8·1 | 6·6 |
| "90%" *ethanol*: | | | |
| $k \times 10^5$ sec$^{-1}$ (0°) | 2·05[19] | 7·32 | 7·60 |
| $k \times 10^5$ sec$^{-1}$ (35°) | | 483 | 523 |
| $\Delta H^{\ddagger}$ | · · | 19·4 | 19·7 |
| $\Delta S^{\ddagger}$ | ·· | 6·3 | 5·3 |

Comparing firstly the solvolysis rate constants in "80%" acetone at 0° (Tables 6 and 7), it is seen that the second *tert.*-butyl group has less of an effect than the second methyl group in increasing the rate constant. The net result is that the Baker–Nathan effect in the rate constants is more pronounced for the dialkyl than for the monoalkyl compounds, a result consistent with the premise that a second *tert.*-butyl group should enhance the shielding to solvation, of the substituted aromatic ring. Comparing heats of activation, it is seen that the heat of activation is significantly lowered by the introduction of a second methyl substituent, from 20·4 ± 0·1 kcal to 20·0 ± 0·1 kcal. Thus the second methyl substituent has the expected effect of further stabilizing the transition state relative to the ground state. By contrast, the introduction of a second *tert.*-butyl group did not decrease the heat of activation. In other words, the effect that the second *tert.*-butyl group should presumably exert in further stabilizing the transition state relative to the ground state, through electron release, is balanced by a factor tending to *decrease* stabilization of the transition state relative to the ground state. This factor could well be steric hindrance to solvation near the substituent. Also in agreement with this interpretation is the fact that the entropy of activation is significantly greater for the di-*tert.*-butyl than for the mono-*tert.*-butyl compound. Note also that both the heat and entropy of activation are greater for the di-*tert.*-butyl than the dimethyl compound.

In "90%" ethanol the results are qualitatively the same as in "80%" acetone, although the differences in kinetic parameters are smaller. As in "80%" acetone, the rate constant in "90%" ethanol is increased more by a second methyl than by a second *tert.*-butyl group. Also, both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are slightly greater for the di-*tert.*-butyl than for the dimethyl compound.

All the solvolysis results, then, find a consistent interpretation in terms of steric hindrance to solvation near the alkyl substituent. On the other hand, the changes in rate constants, heats of activation and entropies of activation brought about by the introduction of a second *meta*-methyl or *tert.*-butyl substituent are difficult to rationalize either in terms of the Baker–Nathan viewpoint or in terms of solvent enhancement of C–H hyperconjugation.