It formed a 2,4-dinitrophenylhydrazone, m.p. 188–190°.

Anal. Calcd. for $C_{20}H_{14}F_2N_4O_6F$: N, 11.76. Found: N, 11.87.

Reactions of I and II with Other Reagents.—These reactions are summarized in Table I. In general, they were very exothermic and were moderated by using diethyl ether or petroleum ether as solvent. The products were usually washed with water and distilled. Regardless of whether the sultone or its rearrangement product was used, the same product was obtained.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WASHINGTON, SEATTLE 5, WASH.]

Alkyl Substituents. VII. Solvent Dependence of the Baker–Nathan Effect in the Solvolysis of *m*-Alkylbenzhydryl Chlorides[1]

BY W. M. SCHUBERT AND ROBERT G. MINTON[2]

RECEIVED MAY 26, 1960

Values of k, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ have been determined conductimetrically for the solvolysis of 3,5-dimethyl- and 3,5-di-*t*-butylbenzhydryl chloride in "80%" acetone and "80%," "87%" and "90%" ethanol. Where literature data were unavailable, kinetic parameters for the solvolysis of benzhydryl chloride and *m*-methyl and *m*-*t*-butylbenzhydryl chloride also were determined. The Baker–Nathan effect on the rate constants has been found to be both temperature and solvent dependent. The changes in kinetic parameters brought about by the introduction of the second *m*-methyl and the second *m*-*t*-butyl groups follow the predictions of the hypothesis that the Baker–Nathan effect is due to steric hindrance to solvation in the vicinity of bulky alkyl substituents.

In chemical transitions in solution that place a high electron demand on an alkyl substituent bonded to an unsaturated system, rate constants tend to take the order Me > Et > *i*-Pr > *t*-Bu.[3,4] This experimental phenomenon has been termed the Baker–Nathan effect. The hypothesis of Baker and Nathan, that this is due to C–H hyperconjugative electron release (in the order of the number of α-hydrogens) becoming predominant over inductive release (in the opposite order)[3,5] when the electron demand placed on the alkyl substituent is sufficiently large, has enjoyed widespread acceptance and stimulated much research.[3,4] However, it has been recognized more recently that the hypothesis is unable to account satisfactorily for a number of facts presumably within its domain and suggestions for its modification[6] or complete replacement[1,7,8] have appeared.

A typical instance of the Baker–Nathan effect is found in the rate constants for the solvolysis of *p*-alkylbenzhydryl chlorides, *e.g.*, in 80% acetone (Table I). Hughes, Ingold and Taher considered these results to be in support of the hypothesis of Baker and Nathan.[9] However, Schubert and Sweeney have pointed out that the orders of the rate constants and heats of activation, as well as the order of the entropies of activation, are equally consistent with their hypothesis that, even in the face of high electron demands, the inherent stabilizing effect of alkyl is in the inductive order, and that steric hindrance to solvation in the vicinity of bulky alkyl groups acts to invert the order of the heats of activation, hence also to invert the rate order.[7,10,11] Direct support for this hypothesis has been found in the principal electronic transition energies of *p*-alkylnitrobenzenes and acetophenones, in the gas phase and in a variety of solvents.[12]

A mild Baker–Nathan effect is found in the rate constants for the solvolysis of *m*-alkylbenzhydryl chlorides in "80%" acetone (Table V)[13] and for the solvolysis of *m*-alkylphenyldimethylcarbinyl chlorides in "90%" acetone.[14] Brown, Brady, Grayson and Bonner, and Berliner and Chen have attributed these results to a slight predominance of C–H hyperconjugative over inductive release from the *m*-position.[15] Schubert and Sweeney have pointed out that these results are equally consistent with mild steric hindrance to ring solvation, acting to invert an inherent inductive order of stabilization of the polar transition state relative to the ground state. It is presumed that a bulky substituent will be less efficient in shielding ring solvation when it is *meta* than when it is *para*. When *meta*, the alkyl group is somewhat removed from the sites of greatest electron deficiency in the ring, *i.e.*, the *o*- and *p*-positions. When *para*, the alkyl group is directly on one of the sites of greatest electron deficiency.

Shiner and Verbanic have observed that for the solvolysis of *m*-methyl- and *m*-*t*-butylbenzhydryl chloride at 0°, the rate constants are in the induc-

---

[1] Preliminary results were reported at the Hyperconjugation Conference, Bloomington, Ind., June 2, 1958; see *Tetrahedron*, **5**, 194 (1959).

[2] National Science Foundation predoctoral Fellow, 1956–1958.

[3] J. W. Baker, "Hyperconjugation," Oxford University Press, London, 1953.

[4] Hyperconjugation Conference, *Tetrahedron*, **5**, 107 (1959).

[5] J. W. Baker and W. S. Nathan, *J. Chem. Soc.*, 1844 (1935).

[6] V. J. Shiner, Jr., THIS JOURNAL, **76**, 1603 (1954); *Tetrahedron*, **5**, 243 (1959).

[7] (a) W. A. Sweeney and W. M. Schubert, THIS JOURNAL, **76**, 4625 (1954); (b) *J. Org. Chem.*, **21**, 119 (1956).

[8] A. Burawoy and E. Spinner, *J. Chem. Soc.*, 3752 (1954).

[9] E. D. Hughes, C. K. Ingold and N. A. Taher, *ibid.*, 949 (1940).

[10] The position taken by these authors has sometimes been misunderstood. They do not maintain that C–H hyperconjugative release is necessarily inoperative; only that the total stabilizing effect of alkyl substituents on electron deficiencies, even when these deficiencies are large, is in the inductive order.

[11] Steric hindrance to solvation acts to raise both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ leading to cancelling effects on the rate constant. It is assumed that $\Delta H^\ddagger/T$ is increased more than $\Delta S^\ddagger$.[7b]

[12] W. M. Schubert, J. Robins and J. L. Haun, THIS JOURNAL, **79**, 910 (1957).

[13] E. Berliner and M. M. Chen, *ibid.*, **80**, 343 (1958).

[14] H. D. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *ibid.*, **79**, 1897 (1957).

[15] It is to be noted that *m*-alkyl substitution increases the rate constant only slightly, much less than does *p*-alkyl substitution. This can be taken as an indication that the electron demand placed on the *m*-alkyl substituent in the transition state is small.

tive order in "90%" ethanol whereas in "66.7%" to "80%" acetone they are in the Baker-Nathan order. This led them to stress also the importance of the role of the solvent in the Baker-Nathan effect. They also determined the influence of these solvents on the rate constants at 0° for the solvolysis of a large number *p*-alkylbenzhydryl chlorides and concluded that the results could be "most readily rationalized in terms of solvent assistance to hyperconjugation and/or steric hindrance to solvation."[11,16,17]

One difficulty in testing the hypothesis of Schubert and Sweeney with kinetic parameters for chemical transitions in solution is that this hypothesis generally makes predictions that parallel those of the hypothesis of Baker and Nathan as originally stated or as modified; *i.e.*, the greater the electron deficiency created in the transition, the more prominent the Baker-Nathan effect.[17] However, it appeared that a comparison of the kinetic parameters for the solvolysis of 3,5-dialkylbenzhydryl chlorides with those for *m*-alkylbenzhydryl chlorides might allow a decision to be made between the various viewpoints. Consequently, the rates of solvolysis of 3,5-dimethyl- and 3,5-di-*t*-butylbenzhydryl chloride have been determined in a number of solvents at at least three temperatures. Rate constants for the solvolysis of benzhydryl chloride and its mono *m*-methyl and *m*-*t*-butyl derivatives also were determined in some of these solvents.

Experimental

3,5-Di-*t*-butylbenzhydrol.—A mixture of 30 g. (0.17 mole) of 3,5-di-*t*-butylbenzoic acid[18] and 60 g. of thionyl chloride was heated to reflux temperature for 1.5 hr. and then distilled, yielding 29.5 g. (91%) of 3,5-di-*t*-butylbenzoyl chloride, b.p. 130–133° (3 mm.). A mixture of the benzoyl chloride (25.3 g., 0.104 mole) and 2 g. of palladium-on-barium sulfate[19] in 100 ml. of dry xylene was heated to reflux temperature and stirred vigorously while a stream of hydrogen was introduced directly over the surface. When hydrogen chloride evolution had ceased the mixture was cooled and the catalyst removed by suction filtration. Distillation of the filtrate yielded a colorless liquid which solidified, b.p. 130–132° (5 mm.). Recrystallization from ethanol–water gave 21.8 g. (82%) of white crystalline 3,5-di-*t*-butylbenzaldehyde, m.p. 82–83°. The 2,4-dinitrophenylhydrazone, red needles, melted at 211–212°.

Anal. Calcd. for $C_{21}H_{26}O_4N_4$: C, 63.30; H, 6.53. Found: C, 62.99; H, 6.47.

A solution of 3,5-di-*t*-butylbenzaldehyde (21.8 g., 0.1 mole) in 100 ml. of dry ether was added over a period of 20 min. to a stirred solution of phenylmagnesium bromide (0.1 mole) in 180 ml. of dry ether and the solution stirred an additional 15 min. A solution of 1 ml. of concd. hydrochloric acid in 10 ml. of water was added dropwise and then the mixture was shaken with 50 ml. of 5% hydrochloric acid. The ethereal layer was washed twice each with water, 5% sodium bicarbonate and water. It was dried over anhydrous sodium sulfate and distilled to give a colorless product, b.p. 172–178° (2 mm.), which solidified in the receiver; yield 22.7 g. Recrystallization three times from pentane gave 15 g. (50%) of fine white needles, m.p. 72–73°.

Anal. Calcd. for $C_{21}H_{28}O$: C, 85.08; H, 9.53. Found: C, 84.89; H, 9.47.

3,5-Dimethylbenzhydrol was prepared from 18 g. (0.13 mole) of 3,5-dimethylbenzaldehyde[20] and 0.15 mole of phenylmagnesium bromide by the same procedure as was used above. Distillation of the crude product, b.p. 148–150° (2 mm.), yielded 12.6 g. of a white crystalline material. It was recrystallized three times from pentane, giving fine white needles, m.p. 50–50.5° (lit.[21] m.p. 50–51°).

Other Benzhydrols.—The procedure of Shiner and Verbanic was used to prepare *m*-methylbenzhydrol and *m*-*t*-butylbenzhydrol.[16] Benzhydrol was obtained commercially (Eastman, white label). To ensure complete purity, each benzhydrol was recrystallized at least three times from pentane: *m*-*t*-butylbenzhydrol, m.p. 52–52.5° (lit.[16] m.p. 53.4°); *m*-*t*-butylbenzhydrol, m.p. 68.5–68.7° (lit.[16] m.p. 67.5–68°); benzhydrol, m.p. 67.5–68°.

Benzyhydryl Chlorides.—The benzhydryl chlorides all were prepared in the same manner. A 15% molar excess of thionyl chloride was added to a solution of the benzhydrol in dry benzene (5 ml. per gram of benzhydrol). The mixture was allowed to stand until gas evolution had ceased and then was heated to reflux temperature for 15 minutes. After removal of excess thionyl chloride and the solvent, the residue was carefully distilled. The middle fraction of the distillate was redistilled just before use. The benzhydryl chlorides all were obtained as colorless liquids: benzhydryl chloride, b.p. 128° (2 mm.); *m*-methylbenzhydryl chloride, b.p. 132° (0.5 mm.); *m*-*t*-butylbenzhydryl chloride, b.p. 149° (0.5 mm.). The 3,5-dimethylbenzhydryl chloride had a boiling point of 146° under 3 mm. pressure (lit.[22] b.p. 143° (0.1 mm.)).

Anal. Calcd. for $C_{15}H_{15}Cl$: C, 78.08; H, 6.55. Found: C, 78.33; H, 6.48.

The 3,5-di-*t*-butylbenzhydryl chloride, a new compound, had b.p. 143° (0.5 mm.).

Anal. Calcd. for $C_{21}H_{27}Cl$: C, 80.10; H, 8.62. Found: C, 79.84; H, 8.50.

Solvents.—The "80%" acetone was prepared by mixing eight volumes (1544 g.) of dry Eastman spectro grade acetone with two volumes (498 g.) of redistilled water at 24°. The "90%," "87%" and "80%" ethanol–water solutions (% by volume) were prepared at 23° from appropriate volumes of redistilled water and anhydrous U.S.P. ethanol fractionated through a 20-plate column. A single batch, carefully protected from the atmosphere, was used to provide the solvent for all the runs in a particular solvent composition.

The Kinetic Method.—Rate measurements at 15°, 25° and 35° were made in an insulated Sargeant bath controlled to within ±0.02° by a Sargeant "Thermonitor" regulating unit. Rate measurements at 0° were made in a large Dewar flask filled with an efficiently stirred ice–water slurry.

Because of its high inherent accuracy, a conductometric method, similar to that of Norris and Morton,[23] was used. A Leeds and Northrup "Jones type" Wheatstone bridge was used to measure the resistance of the solutions; a 1000-cycle alternating current was supplied by a Hewlett and Packard audio oscillator (Cat. no. 4302), the output across the two arms of the bridge was amplified by a Leeds and Northrup amplifier with a 1000-cycle filter (Cat. no. 9847) before it was used to drive the vertical plates of a Heathkit "push–pull type" oscilloscope (model 0–5). The horizontal plates of the oscilloscope were driven directly by the oscillator. All connections were made with shielded coaxial cable; the shields were grounded. This arrangement gives a single line on the oscilloscope which is horizontal when the resistance of the cell and that of the bridge are equal. Readings were taken by presetting a resistance on the bridge and noting the time when the line on the oscilloscope became horizontal.

---

[16] V. J. Shiner, Jr., and C. J. Verbanic, THIS JOURNAL, **79**, 369 (1957).

[17] According to Shiner's hypothesis of solvent assistance to C–H hyperconjugation, the Baker–Nathan effect would be dependent on the ability of the solvent to hydrogen bond with the α-hydrogens of the alkyl substituent, as well as on the degree of electron deficiency created in the substituent. According to the hypothesis of Schubert and Sweeney, the Baker–Nathan effect would be dependent on a similar solvent propensity, namely its ability to solvate the electron deficiencies created in the aromatic ring.

[18] W. Van Hartingsveldt, P. E. Verkade and B. M. Wepster, *Rec. trav. chim.*, **75**, 301 (1956).

[19] E. B. Hershberg and J. Cason, *Org. Syntheses*, **21**, 84(1941).

[20] C. D. Sacklett and H. A. Smith, THIS JOURNAL, **75**, 2654 (1953).

[21] G. Baddeley, S. Varma and M. Gordon, *J. Chem. Soc.*, 4379 (1958).

[22] G. Baddeley and M. Gordon, *ibid.*, 4379 (1958).

[23] J. F. Norris and A. Morton, THIS JOURNAL, **50**, 1795 (1930).

TABLE I

KINETIC PARAMETERS FOR THE SOLVOLYSIS OF BENZHYDRYL CHLORIDES IN "90%" ETHANOL

		$k \times 10^5$ sec.$^{-1}$					
		0.0°	15.0°	25.0°	35.0°	$\Delta H^{\ddagger}$, kcal.[a]	$\Delta S^{\ddagger}$, e.u.[b]
3-Me		3.840	27.43	87.92	...	19.72 ± 0.05	−6.3 ± 0.2
		3.867	27.47	88.40			
		3.883	27.14	87.92			
	Av.	3.86[c]	27.4	88.1			
3-*t*-Bu		4.467	30.86	98.62	...	19.49 ± 0.09	−6.9 ± 0.3
		4.461	30.87	98.15			
		4.440	30.54	98.55			
	Av.	4.46[c]	30.8	98.4			
H-Cpd		2.084	14.57	48.21	146.3	19.78 ± 0.05	−7.3 ± 0.2
		2.067	14.58	48.21	145.3		
		2.074	14.56	48.36	146.6		
	Av.	2.08[c]	14.6	48.3	146.1		
3,5-di-Me		7.408	50.74	162.4	483	19.46 ± 0.05	−6.0 ± 0.2
		7.330	50.74	162.5	480		
		7.317	50.62	163.8	486		
	Av.	7.35	50.7	162.9	483		
3,5-di-*t*-Bu		7.614	53.16	173.6	522.6	19.69 ± 0.05	−5.1 ± 0.2
		7.554	52.51	173.6	522.2		
		7.614	52.66	173.2	525.1		
	Av.	7.59	52.8	173.5	523		

[a] The deviation in $\Delta H^{\ddagger}$ is based on the variation of the slope of the Arrhenius plot within the limits of the standard deviation, *s*. Except for the 3-*t*-Bu compound, the deviation thus calculated was less than ±0.05 kcal. [b] The deviation in $\Delta S^{\ddagger}$ is based on the recorded deviation in $\Delta H^{\ddagger}$. [c] Shiner and Verbanic report the following values of $k \times 10^5$ sec.$^{-1}$ at 0°: k_H 2.05; $k_{Me} = 3.96$; $k_{tBu} = 4.70$[16].

A single piece conductance cell that could be immersed deeply into the water-bath was used. Platinized electrodes were tried but it was found that the conductance of the solutions was not stable after the reaction was complete. The use of shiny electrodes, about 1 cm. apart, eliminated this problem. In check experiments on the conductance of HCl in each of the solvents, it was found that the conductance was linear with the concentration below about 10^{-3} *N* HCl, as also found by Shiner and Verbanic.[16]

The change in conductance with time was measured on about 15 ml. of solution which was 1 to 5 × 10^{-4} molar in benzhydryl chloride. First-order rate constants were obtained from plots of log $(C_\infty - C_t)$ against time, where C_∞ is the steady conductance obtained after greater than nine half-lives and C_t is the conductance at time *t*. The conductance of the solution was recorded at such time intervals that 20–25 readings were generally obtained over the first 1.5 half-lives. The fastest reactions were followed for 2 to 4 half-lives. The first-order plots showed extremely little scatter of the points about a visual line drawn through them. Least squares calculations for ten randomly selected runs gave rate constants to within ±0.2%, with a correlation coefficient in each instance of 0.999^+. The largest difference between a rate constant obtained by least squares and that obtained by visual estimate of the slope of the first-order plot was 0.2%. This was too small a difference to warrant least squares calculation of all the rate constants.

Results

Rate constants were determined in triplicate. The largest deviation of any rate constant from the average was 0.6%, but generally the deviations were much smaller. Values of the heat of activation, $\Delta H^{\ddagger}$, were determined by subtracting *RT* (*T* at 273.16°K.) from the least squares slopes of the Arrhenius activation energy plots of log *k* against $1/T$. Values of $\Delta S^{\ddagger}$ were calculated from the Eyring equation, $k = (kT/h)e^{-\Delta H^{\ddagger}/RT}e^{\Delta S^{\ddagger}/R}$, using the $\Delta H^{\ddagger}$ values obtained and setting T = 273.16° K.

TABLE II

KINETICS PARAMETERS FOR THE SOLVOLYSIS OF BENZHYDRYL CHLORIDES IN "80%" ETHANOL

		$k \times 10^5$ sec.$^{-1}$				
		0.0°	15.0°	25.0°	$\Delta H^{\ddagger}$, kcal.[a]	$\Delta S^{\ddagger}$, e.u.[b]
3-Me		14.39	105.5	340.4	19.92 ± 0.1	−3.0 ± 0.4
		14.46	104.9	339.2		
		14.45	104.4	340.0		
	Av.	14.43	104.9	339.9		
3-*t*-Bu		14.64	103.3	330.4	19.69 ± 0.1	−3.8 ± 0.4
		14.55	103.5	331.5		
		14.58	103.4	332.6		
	Av.	14.59	103.4	331.5		
H-Cpd		8.21	59.94	192.9	19.92 ± 0.1	−4.1 ± 0.4
		8.25	59.34	194.0		
		8.23	59.05	194.0		
	Av.	8.23	59.4	193.6		
3,5-diMe		26.10	181.5	582	19.57 ± 0.1	−3.1 ± 0.4
		26.33	181.0	588		
		25.90	180.5	583		
	Av.	26.1	181.0	584		
3,5-di-*t*-Bu		21.62	159.6	514.5	19.99 ± 0.1	−1.9 ± 0.4
		21.42	158.6	510.9		
		21.70	158.1	512.7		
	Av.	21.58	158.8	513		

[a] The deviation in $\Delta H^{\ddagger}$ is based on the maximum variation found for the slope of the Arrhenius plots within the limits of the standard deviations, *s*. [b] Based on a variation of ±0.1 in $\Delta H^{\ddagger}$.

Observed values of *k*, $\Delta H^{\ddagger}$ and its experimental error, and values of $\Delta S^{\ddagger}$ and its experimental error, are given for the solvents "90%" ethanol, "80%" ethanol, "87%" ethanol and "80%" acetone in Tables I, II, III and IV, respectively. Where literature values are available, these also are listed.

TABLE III

KINETIC PARAMETERS FOR THE SOLVOLYSIS OF BENZHYDRYL CHLORIDES IN "87%" ETHANOL

		$k \times 10^5$ sec.$^{-1}$				
	0.0°	15.0°	25.0°	35.0°[a]	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
3,5-diMe	11.20	75.85	245.5	709.8	19.43 × 0.05[b]	−5.3 ± 0.2[b]
	11.27	76.32	246.0	704.6		
	11.13	76.20	244.5	708.0		
Av.	11.20	76.1	245.3	707		
3,5-di-*t*-Bu	10.81	75.03	247.5	727.5	19.68 ± 0.05[c]	−4.4 ± 0.2[c]
	10.81	75.65	246.0	727.5		
	10.86	75.26	246.4	725.6		
Av.	10.83	75.3	246.6	727		

[a] The runs at 35° had a half-life of about 3 minutes. Though the rate constants are duplicable to good precision, the speed of the reaction may mean they are of doubtful accuracy. [b] The rate constants at 35° were omitted from the calculation.[a] If these are included, the calculated values are: $\Delta H^{\ddagger} = 19.29 \pm 0.4$, $\Delta S^{\ddagger} = -5.8 \pm 1.5$. [c] The rate constants at 35° were omitted from the calculation.[a] If these are included, the calculated values are: $\Delta H^{\ddagger} = 19.58 \pm 0.5$, $\Delta S^{\ddagger} = -4.8 \pm 1.8$.

TABLE IV

KINETIC PARAMETERS FOR THE SOLVOLYSIS OF BENZHYDRYL CHLORIDES IN "80%" ACETONE

		$k \times 10^5$ sec.$^{-1}$				
	0.0°	15.0°	25.0°	35.0°	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
3,5-diMe	0.972	6.339	22.49	72.56	20.02 ± 0.2	−8.0 ± 0.8
	.978	6.369	22.60	72.38		
	.994	6.343	22.54	72.10		
Av.	0.982	6.35	22.5	72.4		
3,5-di-*t*-Bu	0.768	5.313	19.27	63.17	20.43 ± 0. 2	−6.9 ± 0.8
	.789	5.286	18.99	62.86		
	.789	5.280	19.06	62.58		
Av.	0.782	5.29	19.1	62.9		
H-Cpd[a]	0.279	2.20[b]	7.25[c]	...	20.49 ± 0.1	−8.7 ± 0.4
3-Me[a]	.478	3.71[b]	12.2[c]		20.37 ± .1	−8.1 ± .4
3-*t*-Bu[a]	.427	3.29[b]	11.1[c]		20.52 ± .1	−7.8 ± .4
4-Me[d]	8.35		157		18.9	−9.8
4-*t*-Bu[d]	3.59		79.5		20.05	−5.6

[a] Date of Berliner and Chen; for 3-Et, $k \times 10^5$ (0.0°) = 0.428, $\Delta H^{\ddagger} = 20.5 \pm 0.1$, $\Delta S^{\ddagger} = -8.1 \pm 0.5$; for 3-*i*-Pr, $k \times 10^5$ (0.0°) = 0.393, $\Delta H^{\ddagger} = 20.5 \pm 0.1$, $\Delta S^{\ddagger} = -8.6 \pm 0.5$.[13] [b] Data at 15.2°. [c] Data at 25.1°. [d] Data of Hughes, Ingold and Taher[9]; for 4-Et, $k \times 10^5$ (0.0°) = 6.26, $\Delta H^{\ddagger} = 19.4$, $\Delta S^{\ddagger} = -8.6$; for 4-*i*-Pr, $k \times 10^5$ (0.0°) = 4.595, $\Delta H^{\ddagger} = 19.8$, $\Delta S^{\ddagger} = -7.7$.[9]

Discussion

The viewpoint that steric hindrance to solvation of the electron-deficient ring of the transition state in the solvolysis of *m*-*t*-butylbenzhydryl chloride is a factor in modifying the kinetic parameters for this compound leads to certain predictions regarding the effect of a second bulky *t*-butyl group in the other *m*-position of the substituted ring. The second *m*-*t*-butyl group should enhance the solvent shielding of the electron-deficient *p*-position and contribute somewhat to solvent shielding of the other *o*-position. Solvent shielding of the electron-deficient ring of the transition state should be less of a factor in the solvolysis of 3,5-dimethylbenzhydryl chloride. The expectations are that: (1) the introduction of a second *m*-*t*-butyl group, through its steric effect in reducing the heat of solvation of the transition state, should decrease $\Delta H^{\ddagger}$ less than the introduction of the second *m*-methyl and perhaps even increase $\Delta H^{\ddagger}$; (2) the second *t*-butyl group, by sterically reducing the ordering of solvent on the substituted ring of the transition state, should increase $\Delta S^{\ddagger}$ relative to that of the methyl compound; (3) in solvents in which the rate constants for mono *m*-alkyl compounds are in the order $k_{\text{Me}} > k_{t\text{-Bu}}$, this Baker–Nathan effect should become more pronounced for the corresponding dialkyl compounds; and (4) in solvents in which the rate constants for the mono compounds are in the inductive order, *i.e.*, $k_{t\text{-Bu}} > k_{\text{Me}}$, the inductive order should become less pronounced in the di-series, or perhaps the rate constant order might even become inverted in the di-series.[11] These expectations have been fully realized in the four solvents in which the rate studies have been made.

The kinetic parameters for the solvolyses in "90%" ethanol are given in Table I. The rate constants for the *m*-methyl and *m*-*t*-butyl compounds are in the inductive order at all temperatures. The percentage increase in the rate constant is less on the introduction of a second *m*-*t*-butyl group than on the introduction of a second *m*-methyl group. The result is that the inductive order is less pronounced for the di-series; *e.g.*, at 0°, $k_{t\text{-Bu}}/k_{\text{Me}}$ has the value 1.16 for the mono-compounds and 1.03 for the di-compounds. The most interesting changes are in the heats and entropies of activation. As expected, the introduction of a second *m*-methyl slightly decreases $\Delta H^{\ddagger}$. However, the introduction of a second *m*-*t*-butyl group *increases* $\Delta H^{\ddagger}$ beyond the limits of experimental error. In other words, the effect that the second *t*-butyl would be expected to have, that of lowering $\Delta H^{\ddagger}$ by stabilizing the developing carbonium ion of the transition state through electron release, is more than counterbalanced by an effect acting to raise $\Delta H^{\ddagger}$. The introduction of the second *t*-butyl group also raises $\Delta S^{\ddagger}$ beyond the limits of experimental error, whereas $\Delta S^{\ddagger}$ for the dimethyl compound, though slightly lower, is within experimental error of $\Delta S^{\ddagger}$ for the monomethyl compound. These results are completely consistent with the hypothesis of Schubert and Sweeney and difficult to reconcile with the Baker–Nathan concept.

In "80%" ethanol (Table II) the changes in kinetic parameters brought about by the introduction of a second *m*-methyl or a second *m*-*t*-butyl group parallel those found in "90%" ethanol, except that now the rate constants for the dialkyl compounds are in the Baker–Nathan order at all temperatures at which they were determined. The rate constants for the mono-alkyl compounds are in the inductive order (just barely) at 0°, but at 15° and 25° the Baker–Nathan order prevails. The second *m*-methyl substituent *decreases* $\Delta H^{\ddagger}$ slightly but has no significant effect on $\Delta S^{\ddagger}$, whereas the second *t*-butyl substituent *increases* both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ beyond the limits of experimental error. These results find a ready explanation in terms of steric hindrance to ring solvation.

In 80% acetone (Table IV) just as in aqueous ethanol, the rate constant for the solvolysis of benzhydryl chloride is increased only slightly by a single *m*-alkyl substituent (data of Berliner and Chen).[15] This contrasts with the considerable increase in rate brought about by *p*-alkyl substitution (data of Huges, Ingold and Taher). The rate constant for *m*-*t*-butylbenzhydryl chloride is slightly less than for the *m*-methyl compound, *i.e.*, a Baker–Nathan effect is found. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for these compounds are within experimental error of each other and may indicate the operation of opposing factors in approximate balance. The percentage increase in rate on the introduction of either a second *m*-*t*-butyl or a second *m*-methyl group is somewhat greater in 80% acetone than in 80% or 90% ethanol. However, this fact may not be significant since the solvent used for the di-series (prepared on a volume basis) may not have exactly duplicated that used by Berliner and Chen[13] for the mono-series. Even though the solvent composition for the di-series may perhaps differ from that for the mono-series, comparisons are valid of changes in kinetic parameters brought about by the introduction of a second *m*-*t*-butyl group *relative* to those brought about by the introduction of a second *m*-methyl group. As in the other solvents, the introduction of a second methyl increases the rate constant more than the introduction of a second *t*-butyl group, *i.e.*, the Baker–Nathan effect is more pronounced in the dialkyl than in the monoalkyl compounds. The changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ brought about by the introduction of a second *m*-*t*-butyl group relative to those brought about by the second *m*-methyl are within the limits of experimental error. At best they could be considered as showing a trend consistent with the operation of steric hindrance to ring solvation.

The steric hindrance to solvation hypothesis, while it nicely accounts for the changes in kinetic parameters brought about by the substitution of a second *m*-*t*-butyl relative to those brought about by a second *m*-methyl, may not be, of course, the only way in which these results can be explained. Furthermore, questions may be raised about the absolute values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ which are complex composites to which solvation differences between ground and excited states contribute only a part. Nevertheless, the results are indeed difficult to explain in terms of the hypothesis of Baker and Nathan as originally enunciated or as modified to include solvent assistance to C–H hyperconjugation.[16] The results also are not easily accommodated by the hypothesis of Burawoy and Spinner, which attributes the Baker–Nathan effect to steric hindrance to bond shortening.[8]

Isokinetic Temperatures.—Detailed examination of the rate constant data of Tables I and II reveals that the temperature at which the 3,5-dimethyl and 3,5-di-*t*-butyl compounds would have the *same* rate constants, *i.e.*, the "isokinetic temperature,"[24] is below 0° in "90%" ethanol and above 25° in "80%" ethanol. This suggests that a solvent of intermediate composition could be found in which the isokinetic temperature is between 0° and 25°. Interpolation of the rate constants between "80%" and "90%" ethanol led to the expectation that the isokinetic temperature should lie between 0° and 25° in "87%" ethanol. Table III shows that the isokinetic temperature is between 15° and 25° in this solvent. Since $\Delta H^{\ddagger}$ is greater for the 3,5-di-*t*-butyl than for the 3,5-dimethyl compound, the rate constants are in the inductive order above the isokinetic temperature, with the inductive order becoming more prominent as the temperature is increased. Below the isokinetic temperature the rate constants show the Baker–Nathan effect and this becomes more prominent as the temperature is lowered.

The rate constants for the solvolysis of *m*-methyl- and *m*-*t*-butylbenzhydryl chloride in 80% ethanol have an isokinetic temperature between 0° and 15° (Table II). Since $\Delta H^{\ddagger}$ is greater for the *m*-methyl than for the *m*-*t*-butyl compound, the rate constants are in the inductive order below the isokinetic temperature and in the Baker–Nathan order above it. This contrasts with the results for the dialkyl compounds, for which the rate constants are in the Baker–Nathan order below the isokinetic temperature and in the inductive order above it.

These results illustrate the risk of making conclusions about the potential energy effects of structural changes on the sole basis of small differences in rate of equilibrium constants, a matter to which Leffler has directed his attention.[24] The results also point out the desirability of determining heats and entropies, especially when rate or equilibrium constants differ by just small amounts.

In alcohol–water mixtures, the Baker–Nathan

---

[24] J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

effect in these and other solvolyses reactions becomes more prominent as the water percentage of alcohol-water solutions is increased.[16] It also is prominent in "80%" acetone. This is to be expected, on the basis that solvation of the electron-deficient ring of the transition state should tend to become more important, and hence more sensitive to steric shielding, as the water content of the solvent is increased.[17,25] It is interesting to note that as the alcohol percentage is decreased. the heats of activation tend to increase slightly, rather than decrease (Tables I, II and III). Thus the general increase in rate accompanying a decrease in alcohol percentage is due to an increase in the entropy of activation. Both the increase in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with increasing water content of the ethanol-water solvents may be a reflection of the fact that those solvent molecules that participate in solvating the highly polar transition state (perhaps preferentially water molecules) are in the ground state more tightly associated with neighboring solvent molecules in the more aqueous solvent mixture. The lower rates in "80%" acetone (Table IV) are mainly due to a less favorable, more negative, entropy of activation. Perhaps this means that solvent association is less rigid in this medium.

Acknowledgment.—The authors wish to express their appreciation to the Office of Ordnance Research, United States Army, for partial support of this research.

---

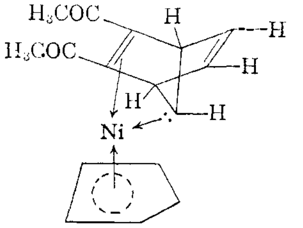
[25] The Baker–Nathan effect in the principal electronic transition energies of *p* alkylnitrobenzenes and acetophenones is found only in polar basic solvents and is more prominent in water than in various alcohols.[18]

COMMUNICATIONS TO THE EDITOR

THE SYNTHESIS OF [2,3-BIS-(METHOXYCARBONYL)-2π,5-NORBORNADIEN-7-YL](π-CYCLOPENTADIENYL) NICKEL(II)[1]

Sir:

A new class of nickel complexes has been discovered as a result of the reaction of dicyclopentadienylnickel with dimethyl acetylenedicarboxylate. In a previous communication[2] it was reported that acetylene reacted with dicyclopentadienylnickel to form the binuclear nickel complex bis-(cyclopentadienylnickel)-acetylene. Recently, it has been found that substitution of electron withdrawing groups about the acetylenic bond altered the electronic distribution about the bond to such an extent that binuclear nickel complexes were not formed as major products of reaction with dicyclopentadienylnickel. Thus, when dimethylacetylene dicarboxylate was contacted with dicyclopentadienylnickel a bright orange-red air stable solid, m.p. 84°, was isolated which possessed an elemental composition and a molecular weight indicative of a simple bimolecular coupling of the two reactants. On the basis of its diamagnetism,[3] n.m.r. data and degradative studies, structure I is proposed for the new complex.



I

The complex was prepared by contacting a solution of 2.0 g. (0.011 mole) of dicyclopentadienylnickel with 1.5 g. (0.011 mole) of dimethyl acetylenedicarboxylate in 25 ml. of tetrahydrofuran at room temperature for 65 hours under a protective atmosphere of pure nitrogen. The solvent was removed under reduced pressure at room temperature and the residue was relieved of 0.6 g. of unreacted dicyclopentadienylnickel by sublimation at 40° and 0.02 mm. The remaining residue was extracted with hot low boiling petroleum ether and the orange extracts were filtered. Concentration of the filtrate caused the crystallization of 1.7 g. of a dark red solid which was purified by recrystallizations from methanol and low boiling petroleum ether to yield an orange red solid, m.p. 84° (calcd. for $C_{16}H_{16}O_4Ni$: C, 58.1; H, 4.87; Ni, 17.7; mol. wt., 331. Found: C, 57.9; H, 4.88; Ni, 17.4; mol. wt., 326. The yield of product based on consumed dicyclopentadienylnickel was 68%.

Hydrogenation of the complex in ethanol over platinum at atmospheric pressure and room temperature caused complete decomposition to metallic nickel, cyclopentane and dimethyl *endo-cis*-2,3-norbornanedicarboxylate, m.p. 55°. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60; found: C, 62.3; H, 7.55. The organic fragments were isolated in yields of 70 and 60%, respectively. The identity of cyclopentane was established by comparing it with an authentic sample with vapor phase chromatographic and mass spectrometric techniques. An authentic sample of dimethyl-*cis-endo*-2,3-norbornanedicarboxylate was prepared by a Diels–Alder addition of dimethyl acetylenedicarboxylate and cyclopentadiene and then reduction over platinum. The degradative sample and the synthesized material were identical, having superimposable infrared spectra and identical melting points separately or mixed. The above results indi-

---

[1] Presented before the 138th meeting of the American Chemical Society, New York, N. Y., Sept., 1960.

[2] M. Dubeck, *J. Am. Chem. Soc.*, **82**, 502 (1960).

[3] I am indebted to Dr. Stanley Kirschner, Wayne State University, for the magnetic susceptibility measurements.