Electrochemical and Spectroscopic Studies of Cation Radicals. I.
Coupling Rates of 4-Substituted Triphenylaminium Ions

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Data are presented on the electrochemically determined coupling rates of 21 mono-para-substituted triphenylaminium cation radicals in acetonitrile at platinum. There is a definite trend in coupling rate as a function of substituent; *i.e.*, there appears to be a Hammett-type relationship. Most substituent effects can be adequately described by σ^+ values from carbonium ion reactions with the exception of strong electron-donating functional groups. These substituents lend enhanced stabilization to cation radicals above that in carbonium ions. These data are intended to serve as a basis for further electrochemical and spectroscopic studies into the effects of substituents on cation radical stabilities.

Cation radicals as acknowledged entities are relative newcomers to the field of organic chemistry. In the past few years, their presence has been confirmed in an ever-increasing number of electroorganic oxidations. In fact, data are accumulating at such a rate that the future may see the cation radical cited as the primary intermediate in organic electrooxidations. Due to their present and projected importance, it would seem desirable to acquire data that would characterize the behavior of these species as a whole. Of primary importance is the effect of substituents upon cation radical stabilities; substituent effects in unoxidized molecules have been extensively, if not completely, characterized. However, the paucity of data for cation radicals is striking but understandable due to their relatively short chemical history. This communication is the first of a series that is intended to help alleviate this information gap.

In studying substituent effects on cation radical properties, one might anticipate Hammett-type behavior, *i.e.*, a linear relationship between various radical properties and substituent reactivity constants assigned to the various functional groups. Initially, one would attempt to correlate radical properties with σ^+ values, reactivity parameters pertinent to carbonium ion reactions. Hopefully, the existing σ^+ values might apply within the limits of experimental error to the cation radical systems. If this were not the case, then a new series of substituent reactivity constants would have to be obtained from empirical data to fit the properties of cation radicals.

The assumption of Hammett-type behavior, even in a qualitative sense, for cation radicals is at present questionable. In fact, Walter has proposed non-Hammett behavior for a series of triarylaminium cation radicals based on epr and visible absorption spectra,[2] with an LCAO-MO treatment to back up the experimental data. However, contradictory spectral data have been presented on both triarylaminium cation radicals[3] and para-substituted *N,N*-dimethylanilinium radicals[4] which indicate that the behavior of arylaminium cation radicals may obey the Hammett relationship at least in a qualitative sense. In view of this controversy over the available spectral data, it was felt that electrochemical studies would be more reliable as a starting point;

once a firm basis were established difficulties with spectral data could, hopefully, be resolved. Certainly, a truly reliable set of substituent parameters should apply to spectral as well as electrochemical data.

In the electrochemical oxidation of triphenylamines in acetonitrile, it has been proposed that the initial step is the formation of the cation radical; two of these then couple in solution to form a substituted tetraphenylbenzidine (TPB).[5,6] Quantitative data have been obtained for several 4-substituted triphenylamines in the form of second-order coupling rate constants, and it was generally found that electron-donating substituents tended to stabilize the cation radicals while electron-withdrawing groups had the opposite effect.[7-9] Even based on the behavior of the relatively few derivatives for which quantitative data were obtained it was obvious that the substituents were exerting a large effect on the rate constant in a predictable fashion; hence, it was hoped that these systems would serve as a sensitive probe for studying substituent effects upon cation radical properties.

Experimental Section

The coupling rate constants were determined using either chronoamperometry or rotating disk voltammetry, the former for systems with relatively slow coupling rates and the latter for those with rapid decomposition of the cation radicals. These two techniques complement one another nicely, since chronoamperometry is useful in the second-order rate constant range of 10^{-1} to 10^3 mol^{-1} sec^{-1} and rotating disk is usable over the range of 10^3 to 10^8. The instrumentation for chronoamperometric studies was standard; that for rotating disk voltammetry employed "rotoamperometry" for rapid data acquisition.[10]

In the triphenylamine systems, the kinetic behavior does not strictly fit any of the extreme cases for which digital simulation working curves are available.[8,9] However, the $K = 0/0$ case best approximates these systems; so it was chosen. In this case one is assuming that there are no ECC complications (*i.e.*, amine cation radical oxidizing the benzidine parent) competing with the purely electrochemical steps. Since the $E°$'s for the amine and benzidine couples are always fairly close, this seems a reasonable assumption. Also, since all the working curves nearly coincide over a fairly wide range of N_{app}, selection of a particular working curve is not critical if one works on this coincidental portion.

In Table I, the digital output of the chronoamperometric

(1) Correspondence should be addressed to the University of Idaho.

(2) R. I. Walter, *J. Amer. Chem. Soc.*, **88**, 1923, 1930 (1966).

(3) M. Mohammad and B. R. Sundheim, *Theor. Chim. Acta*, **10**, 222 (1968).

(4) B. M. Latta and R. W. Taft, *J. Amer. Chem. Soc.*, **89**, 5172 (1967).

(5) R. F. Nelson, Ph.D. Thesis, Kansas University, 1966.

(6) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, and R. N. Adams, *J. Amer. Chem. Soc.*, **88**, 3498 (1966).

(7) R. F. Nelson and R. N. Adams, *ibid.*, **90**, 3925 (1968).

(8) L. S. Marcoux, R. N. Adams, and S. W. Feldberg, *J. Phys. Chem.*, **73**, 2611 (1969).

(9) R. F. Nelson and S. W. Feldberg, *ibid.*, **73**, 2623 (1969).

(10) S. C. Creason and R. F. Nelson, *J. Electroanal. Chem.*, **27**, 189 (1970).

TABLE I
DIGITAL FORM OF THE CHRONOAMPEROMETRIC WORKING CURVE FOR THE MECHANISM

$$A \underset{}{\overset{1e^-}{\rightleftharpoons}} B; \quad 2B \overset{k}{\longrightarrow} C; \quad C \underset{}{\overset{2e^-}{\rightleftharpoons}} D$$

$N_{app}{}^a$	Log $ktC_A{}^b$	N_{app}	Log ktC_A
1.028	−1.699	1.720	0.301
1.036	−1.599	1.753	0.401
1.044	−1.499	1.782	0.501
1.055	−1.399	1.806	0.601
1.068	−1.299	1.826	0.701
1.084	−1.199	1.844	0.801
1.104	−1.099	1.858	0.901
1.128	−0.999	1.871	1.001
1.156	−0.899	1.882	1.101
1.189	−0.799	1.891	1.201
1.227	−0.699	1.900	1.301
1.270	−0.599	1.908	1.401
1.317	−0.499	1.915	1.501
1.369	−0.399	1.921	1.601
1.423	−0.299	1.927	1.701
1.479	−0.199	1.932	1.799
1.534	−0.099	1.937	1.899
1.587	0.001	1.942	1.998
1.636	0.101	1.946	2.098
1.680	0.201	1.950	2.198
		1.954	2.298

^{a} N_{app} = apparent number of electrons per molecule at any time during the electrochemical process, or $(it^{1/2}/C_A)_{\text{kinetic}}/(it^{1/2}/C_A)_{\text{one-eletron}}$. ^{b} t = electrolysis time for the corresponding value of N_{app}; C_A = initial concentration of parent amine.

SCHEME I
ANODIC OXIDATION PATHWAY FOR 4-SUBSTITUTED TRIPHENYLAMINES

working curve used is presented for convenience. The same type of data for other working curves is available upon request.

A more serious consideration is that the slopes of the working curves become very small at the extremes so that a slight error in determining N_{app} is magnified tremendously in calculating the rate constant. In practice, it appears that the chronoamperometric working curves are only quite reliable between N_{app} values of 1.15–1.60, where the slope is relatively large. Therefore, it was necessary to juggle concentration of the amine and the measurement time gate to get within this region on the working curve.

Another thorny experimental problem was estimation of one-electron values for the various derivatives. This was not difficult for the systems with slow radical decomposition rates since the first electrochemical step could be readily monitored at low amine concentrations and short time gates. For the other systems, one-electron values had to be estimated from calculated diffusion coefficients[9] and from long time gate experiments and high amine concentrations (where the ECE process proceeds essentially to completion) for chronoamperometric studies; for rotating disk work, one-electron values could be readily obtained for all the compounds investigated.

In acetonitrile–0.1 F tetraethylammonium perchlorate (TEAP), the solvent system used for this work, the maximum time allowable for running current–time curves was found to be about 8 sec. After this time convection usually sets in, thus distorting the curves. At short times (0.1–0.6 sec) large background corrections were necessary on low-concentration runs, making work in this range difficult at best. Background corrections were often not necessary, but they were carried out for all runs.

The values listed for the second-order coupling rate constants are averages of from 6 to 12 runs on each compound; the uncertainties listed are the extreme variations from the average values. Runs were carried out over at least a tenfold variation in concentration for each compound to detect a concentration-dependent variation of k; none was found. Although there were variations in the rate constants with concentration, they were generally random. As mentioned, it was found that the best results were obtained when operating on the linear portions of the working curves, that is between N_{app} values of 1.15 to 1.60. A good deal of the deviation in the measurements accrued from working outside this region.

In all these systems, benzidines are formed from the triphenylamines by intermolecular coupling (*vide infra*). In some cases,
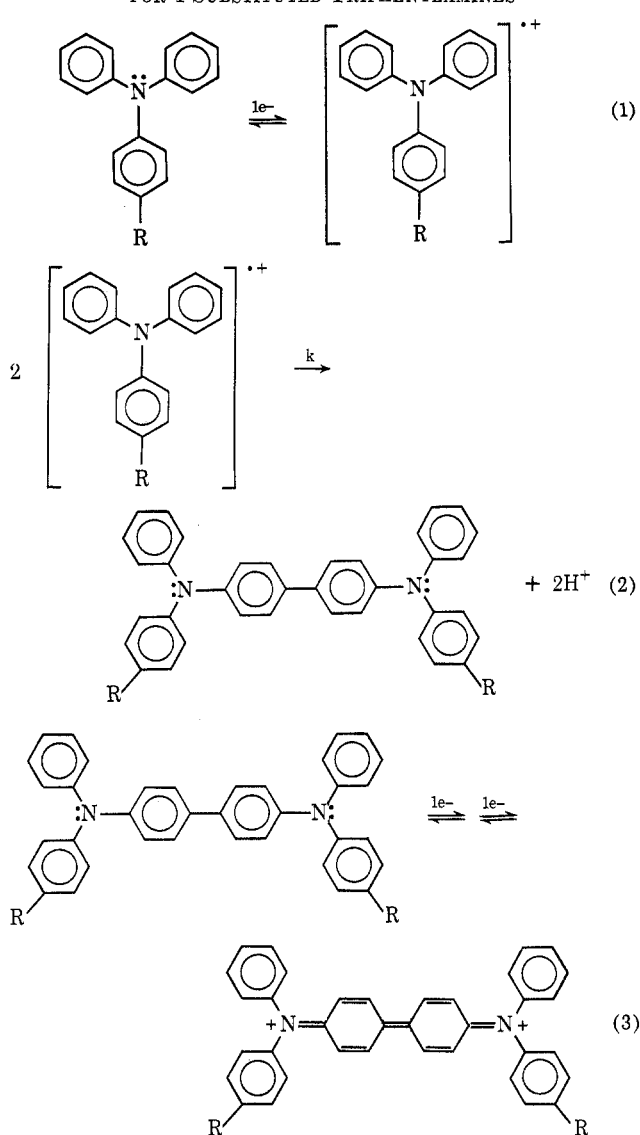
the benzidines formed have been previously characterized;[7] for a number of other amines generation of the corresponding benzidines was verified by electrochemical and spectroscopic methods, as well as by chemical isolation. For all systems controlled-potential electrolyses were carried out, and the presence of the corresponding benzidines was confirmed both electrochemically and spectroscopically in solution; in all cases the amount of benzidine formed was at least 90% of the anticipated amount, with the exception of the methylthio derivative (*vide infra*).

Based on these experiments, it is felt with reasonable certainty that no extraneous chemical complications are affecting the processes shown in Scheme I during the time scales involved in the chronoamperometric and rotating disk experiments (8–30 sec).

All measurements were conducted at 22 ± 1° in a one-compartment cell. Platinum button electrodes were employed for both rotating disk and chronoamperometry studies with a platinum wire auxiliary and sce reference. The $E_{1/2}$ values were obtained from rotating disk voltammograms at rotation rates where the chemical follow-up reaction would be completely outstripped. This was possible in all cases in the rotation range of 2000–8000 rpm. These values, then, are *true* $E_{1/2}$'s not shifted by associated chemical reactions.

Compound preparation was straightforward in all cases. Triphenylamine itself was Eastman White Label and was recrystallized from methanol.

In many cases, the substituted triphenylamines were prepared by Ullmann reactions using either 1 mol of para-substituted

TABLE II

PREPARATIVE DATA ON 4-SUBSTITUTED TRIPHENYLAMINES
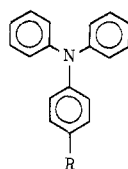
R	Registry no.	Method of preparation	Recryst medium	Mp, °C	Lit mp, °C (ref)
OCH₃	4316-51-2	Ullmann reaction	Hexane	104–105	104 (15)
OC₂H₅	4316-52-3	Ullmann reaction	Ethanol–hexane	89–90[a]	
OC₆H₅	36809-17-3	Ullmann reaction	Benzene–hexane	107–108[a]	
SCH₃	36809-18-4	Ullmann reaction	Hexane	83–84[a]	
NHCOCH₃	4316-77-2	Ullmann reaction	Methanol–water	199–201	195 (16)
C₆H₅	4432-94-4	Ullmann reaction	Methanol	109–110	110 (17)
CH₃	4316-53-4	Ullmann reaction	Methanol	68–69	68–69 (18)
C₂H₅	36809-22-0	Ullmann reaction	Ethanol–hexane	53–54[a]	
t-C₄H₉	36809-23-1	Ullmann reaction	Heptane	52–53[a]	
H	603-34-9	Commercial product	Methanol	126–127	
F	437-25-2	Ullmann reaction	Ethanol–hexane	101–102	98–98.5 (19)
Cl	4316-56-7	Ullmann reaction	Hexane	108–109	106–107 (20)
Br	36809-26-4	Bromination of triphenylamine	Heptane	112–114	94–96 (11)
COOCH₃	25069-30-1	Ullmann reaction	Acetonitrile	86–87	88 (23)
CHO	4181-05-9	Formylation of triphenylamine	Ethanol	132–134	132–133.5 (13)
COCH₃	1756-32-7	Ullmann reaction	Benzene–ethanol	138–140	142–143 (21)
COC₆H₅	16911-33-4	Ullmann reaction	Benzene–hexane	126–127	127–128 (22)
SO₂N(C₂H₅)₂	36809-31-1	Ullmann reaction	Benzene–ethanol	91–93	
CF₃	36809-32-2	Ullmann reaction	Benzene–heptane	104–105	
CN	20441-00-3	Ullmann reaction	Ethanol	126–127	126–127 (7)
NO₂	4316-57-8	Nitration of triphenylamine	Methanol	140–142	139–142 (14)

[a] New compound. Analytical data show C, H, and N analyses within ±0.4% of theoretical values: Ed.

aniline and 2 mol of iodobenzene or mole-per-mole amounts of diphenylamine and the appropriate para-substituted iodobenzene. The reactions were run at about 200° for 12–18 hr; potassium carbonate was added to take up the HI liberated, and copper powder was used as a catalyst. No solvent was used in most cases; when the reaction mass would solidify, a few milliliters of xylene was added. It was found that the elimination of solvent from the reaction increased the yields considerably over earlier syntheses. Yields of 40–80% were routinely achieved using the above conditions.

The hot reaction mixtures were extracted with hexane whenever possible, benzene being used in alternate cases; the extraction liquids were then chromatographed on Woelm neutral alumina with hexane or benzene using a column with a diameter of 20 mm and a length of 300–400 mm. Recrystallizations were effected from various media; these data, along with uncorrected melting points, are presented in Table II. Completion of the Ullmann reactions and formation of the desired products were verified by electrochemical behavior and infrared spectra (absence of N–H peak), as well as by CHN analyses.

Three of the amines were prepared by direct substitution reactions. Bromination with *N*-bromosuccinimide in dry benzene yielded 4-bromotriphenylamine,[11,12] and triphenylamine-4-aldehyde was prepared by formylation of triphenylamine with *N,N*-dimethylformamide and phosphoryl chloride.[13] 4-Nitrotriphenylamine was prepared by nitrating triphenylamine with a nitric acid–acetic acid mixture using the procedure of Herz.[14] The product was chromatographed on Woelm neutral alumina with benzene–ether and recrystallized from methanol. Physical

data were available for a number of other derivatives;[15–23] for those compounds not previously reported CHN analyses were run, and the precentages agreed with calculated values to within ±0.4%.

Hückel molecular orbital calculations employed parameters used previously.[7]

σ^+ values were used for all substituents for which values were available; these data were taken from the compilation of Brown and Okamoto.[24] Where σ^+ constants were not available, σ values were used; these were extracted from a standard source.[25] The σ^+ values chosen are for para-substituted derivatives. In the case of these coupling reactions, where the coupling site is far removed from the substituents, this choice is open to question. However, the open para positions are, in fact, in conjugation with the substituents through the amine nitrogen and, as evidenced by the large variation in the coupling rate constant with substituent, the extent of conjugation is considerable.

Results and Discussion

The anodic oxidations of 4-substituted triphenylamines have been proposed to go by the pathway shown in Scheme I. The only aspect of the mechanism that is

(11) M. F. Abdel-Wahab and M. Z. Barakat, *Monatsh. Chem.*, 88, 692 (1957).

(12) L. Horner, E. Winkelmann, K. H. Knapp, and W. Ludwig, *Chem. Ber.*, 92, 288 (1959).

(13) T. N. Baker, III, W. P. Doherty, Jr., W. S. Kelley, W. Newmeyer, J. E. Rogers, Jr., R. E. Spalding, and R. I. Walter, *J. Org. Chem.*, 30, 3714 (1965).

(14) R. Herz, *Chem. Ber.*, 23, 2537 (1890).

(15) H. Wieland and E. Wecker, *ibid.*, 43, 699 (1910).

(16) S. Gambarjan, *ibid.*, 41, 3507 (1908).

(17) J. Piccard and F. de Montmollin, *Helv. Chim. Acta*, 6, 1011 (1923).

(18) R. J. B. Marsden, *J. Chem. Soc.*, 627 (1937).

(19) N. J. Leonard and L. E. Sutton, *J. Amer. Chem. Soc.*, 70, 1564 (1948).

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(21) C. J. Fox and A. L. Johnson, *J. Org. Chem.*, 29, 3536 (1964).

(22) B. Staskun, *ibid.*, 33, 3031 (1968).

(23) H. Hartmann and W. Kleinpaul, *Z. Phys. Chem. (Frankfurt am Main)*, 25, 415 (1960).

(24) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 80, 4979 (1958).

(25) C. D. Ritchie and W. F. Sager, in "Progress in Physical Organic Chemistry," Vol. 2, S. F. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience, New York, N. Y., 1964, pp 334–337.

Table III

Electrochemical Data on 4-Substituted Triphenylamines

No.	Substituent	$E_{1/2}{}^a$	n value[b]	$\sigma^+ (\sigma)^c$	k, mol^{-1} sec^{-1}
1	OCH_3	0.79	1.98	−0.78	$6 \pm 2 \times 10^{-1}$
2	OC_2H_5	0.80	2.01	−0.78	$8 \pm 3 \times 10^{-1}$
3	$NHCOCH_3$	0.82	2.02	−0.6	1.5 ± 0.4
4	OPh	0.87	2.02	−0.5	4.0 ± 1.0
5	SCH_3	0.82	0.97		
6	CH_3	0.90	1.99	−0.31	$9.0 \pm 1.0 \times 10^1$
7	C_2H_5	0.89	2.03	−0.30	$1.0 \pm 0.1 \times 10^2$
8	$t\text{-}C_4H_9$	0.91	2.06	−0.26	$1.0 \pm 0.1 \times 10^2$
9	C_6H_5	0.92	2.10	−0.18	$6.0 \pm 0.6 \times 10^1$
10	F	1.04	2.03	−0.07	$5.0 \pm 0.8 \times 10^2$
11	H	1.00	2.02	0.00	$1.2 \pm 0.4 \times 10^3$
12	Cl	1.05	1.94	0.11	$6.5 \pm 1.3 \times 10^2$
13	Br	1.05	1.96	0.15	$1.4 \pm 0.3 \times 10^3$
14	$COCH_3$	1.16	2.01	(0.50)	$2.6 \pm 0.7 \times 10^3$
15	COC_6H_5	1.16	2.03	(0.50)	$3.0 \pm 0.9 \times 10^3$
16	$COOCH_3$	1.15	2.00	0.48	$3.3 \pm 1.0 \times 10^3$
17	CHO	1.18	2.04	(0.22)	$4.7 \pm 1.5 \times 10^3$
18	CF_3	1.17	2.07	(0.54)	$6.4 \pm 2.0 \times 10^3$
19	$SO_2N(C_2H_5)_2$	1.17	2.06	(0.57)	$7.2 \pm 2.3 \times 10^3$
20	CN	1.22	2.05	(0.66)	$1.0 \pm 0.3 \times 10^4$
21	NO_2	1.25	2.02	(0.79)	$1.4 \pm 0.4 \times 10^4$

a Values taken from rotating disk voltammograms. *b* These data were obtained by controlled-potential coulometry of roughly millimolar solutions. *c* Numbers in parentheses are σ values; others are σ^+.

open to serious question is whether the coupling step occurs *via* a radical–radical or radical–parent pathway. The experimental data available suggest very strongly that it is indeed a radical–radical coupling reaction.[9]

This being the case, then, the variation in the coupling rate constant as a function of the substituent in the 4 position should yield definitive information regarding the effects of functional groups on cation radical stabilities. The coupling rates are presented in Table III along with some standard electrochemical data. In all cases, n values of 2.0 ± 0.1 were obtained; this is what one would anticipate if the amines were being quantitatively transformed to the corresponding benzidines with no further chemical complications present. The only exception to this was the methylthio derivative, which does not form the corresponding benzidine upon oxidation. The product formed has not been identified, but it is significant to note that the decomposition rate for the cation radical of this species is quite slow, about that of the alkoxy derivatives. Thus, one can say that, qualitatively, the methylthio group tends to lend considerable stabilization to the triphenylamine cation radical. This marked stabilization for cation radical species by the methylthio group has been noted in other systems; [26,27] so it appears to be a general phenomenon.

In Figure 1, the data are plotted as log k *vs.* σ^+ or σ. The only alteration from the values given in Table III is for triphenylamine itself to correct for the fact that there are more coupling sites available for this molecule than for the others having a single para substituent. Thus, for two 4-substituted triphenylaminium cation radicals there are four possible coupling site combinations while for the triphenylaminium radical itself there are nine. Because of this, the k value for triphenylamine in Table III was multiplied by $^4/_9$ for plotting in Figure 1. The numbers in the diagram correspond to

(26) A. K. Carpenter and R. F. Nelson, unpublished data.
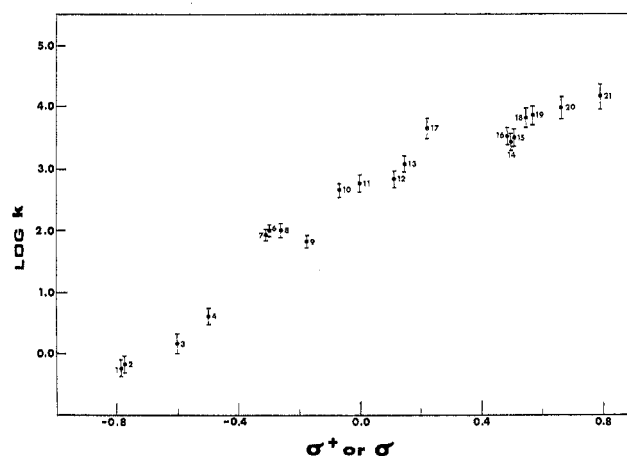(27) A. Zweig and J. E. Lehnsen, *J. Amer. Chem. Soc.*, **87**, 2647 (1965).

Figure 1.—Plot of second-order coupling rate constants *vs.* Hammett substituent constants. Numbered points correspond to those in Table III. Points 1 and 2 are slightly offset to avoid confusion in the presentation of error limits.

the various substituents as listed in Table III, as are the uncertainty limits.

A straight line is not included in Figure 1 because of the scatter in several of the points. A hypothetical line with little scatter could be drawn through points 6–8, 10–16, and 18–21. Using these points, a plot of log k_x/k_0 *vs.* σ^+ yields a ρ value of 2.0. This substantial value reflects the marked effect of substituent on the coupling rate. A plot using only σ values showed a great deal more scatter than the data in Figure 1 and in particular compounds 1–4 were a good deal to the right of their positions in Figure 1. The better agreement with σ^+ than with σ values for the electron-donating substituents is indicative of a polar transition state (the cation radical) which is stabilized by strong electron-donating substituents.

It is noteworthy that points for compounds 1–4, all containing strong electron-donating functional groups, lie below the hypothetical line. This infers that the

σ^+ values available for carbonium ion reactions are not sufficiently negative to account for the stabilization of cation radicals by these substituents. It has been shown that methoxy groups do indeed stabilize carbonium ions by resonance stabilization due to charge localization on the substituent;[28] in free radicals, however, it has recently been demonstrated that methoxy group stabilization is small.[29] In cation radicals, it appears that the stability of the radical depends on keeping the unpaired electron density at the potential reaction site minimal. Therefore, resonance forms where the unpaired electron is localized at other positions will contribute to enhanced stability.

Two points need to be rationalized, namely, the facts that strong electron donors lend stabilization to the cation radicals above that present in carbonium ions and the apparent fact that electron-withdrawing groups have little or no additional effect on cation radicals relative to carbonium ions. For the first point, it is instructive to consider the resonance forms that can be reasonably drawn for the 4-methoxytriphenylaminium radical cation and the 4-methoxytriphenylmethyl carbonium ion as shown in Chart I. Resonance forms not involving the substituted rings are not shown since they would always be equivalent. Forms I–IV for the cation radical, where the unpaired electron and positive charge are localized on the central nitrogen and the ring positions ortho and para to it, are matched by forms I–IV for the carbonium ion. Forms V for each are also reasonably substantial contributors since the methoxy group can readily accommodate the positive charge and unpaired electron. In the cation radical, forms VI–VIII show the charge on the oxygen and the unpaired electron ortho and para to the methoxy group. Equivalent forms for the carbonium ion such as VI would require an unreasonable triplet state configuration; VII and VIII are not shown, but the same reasoning would apply. Clearly, the cation radical would be predicted to be considerably more stable based on consideration of these resonance forms. The remarkable stabilization of these cation radical systems by strong electron donors is further verified by the fact that the coupling rate for 4-dimethylaminotriphenylamine is so slow as to be immeasurable;[30] thus, this substituent stabilizes the radical to such an extent that decomposition is negligible. This is to be anticipated, since the unpaired electron and positive charge would be fairly equally divided between the two amine nitrogens.

The same type of comparison is shown in Chart II for the corresponding nitro derivatives. Here, forms I–IV are again equivalent for both, and when further electron distributions such as V and VI for the cation radical and V for the carbonium ion are considered, one sees that any further resonance effect would not be anticipated in either case. The net effect is that the strong electron-donating substituents, acting as ortho–para directors, spread the electron density around the substituted ring at the expense of the unsubstituted rings. The electron-withdrawing groups, acting as meta directors, only overlap the effect of the amine nitrogen and thus the electron density in the unsubstituted rings is proportionately higher. This is shown pictorially below

(28) Y. Okamoto and H. C. Brown, *J. Amer. Chem. Soc.*, **79**, 1909 (1957).
(29) J. W. Timberlake and M. L. Hodges, *Tetrahedron Lett.*, 4147 (1970).
(30) R. F. Nelson, unpublished data.

CHART I

RESONANCE FORMS FOR THE
4-METHOXYTRIPHENYLAMINIUM CATION RADICAL AND THE
4-METHOXYTRIPHENYLMETHYL CARBONIUM ION

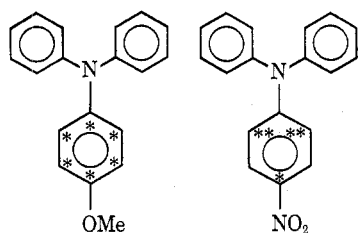Cation Radical

Carbonium Ion
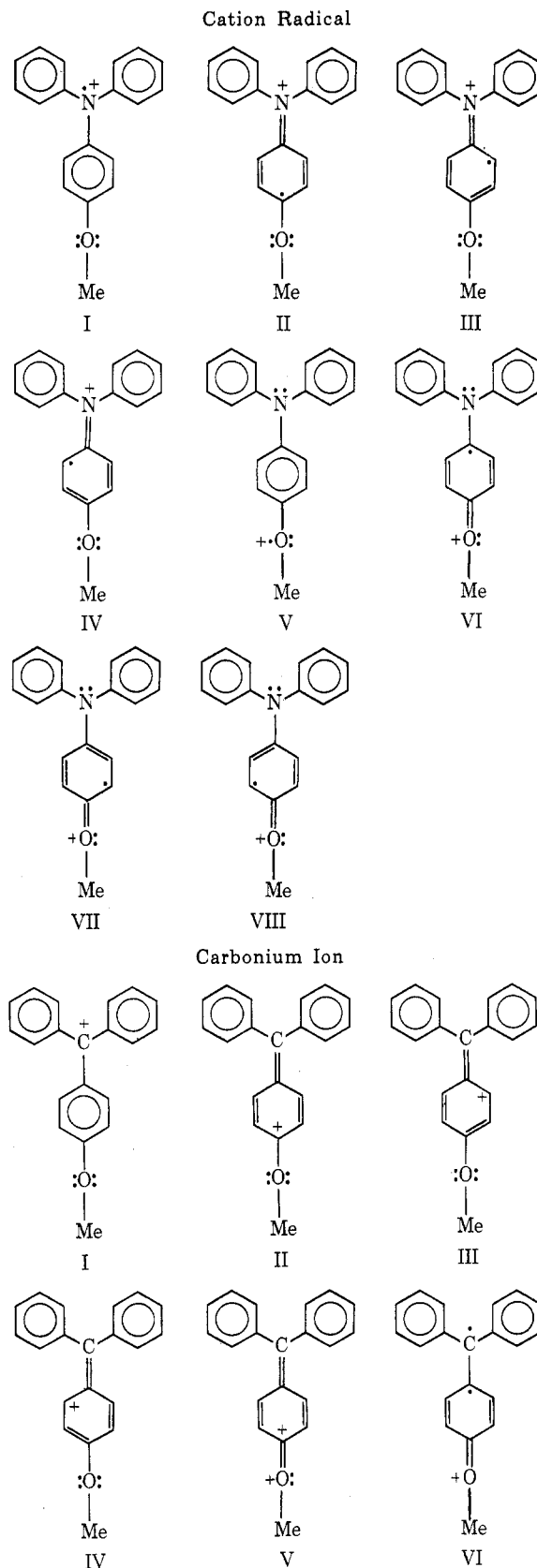
with the directing power of each substituent shown by asterisks. The same picture can be gleaned from HMO calculations with electron densities represented by the

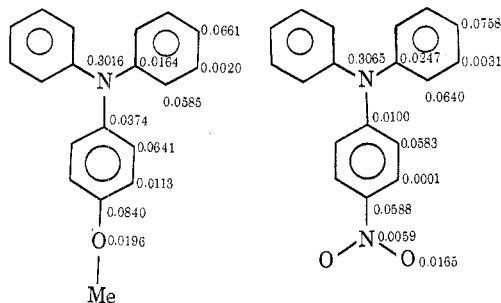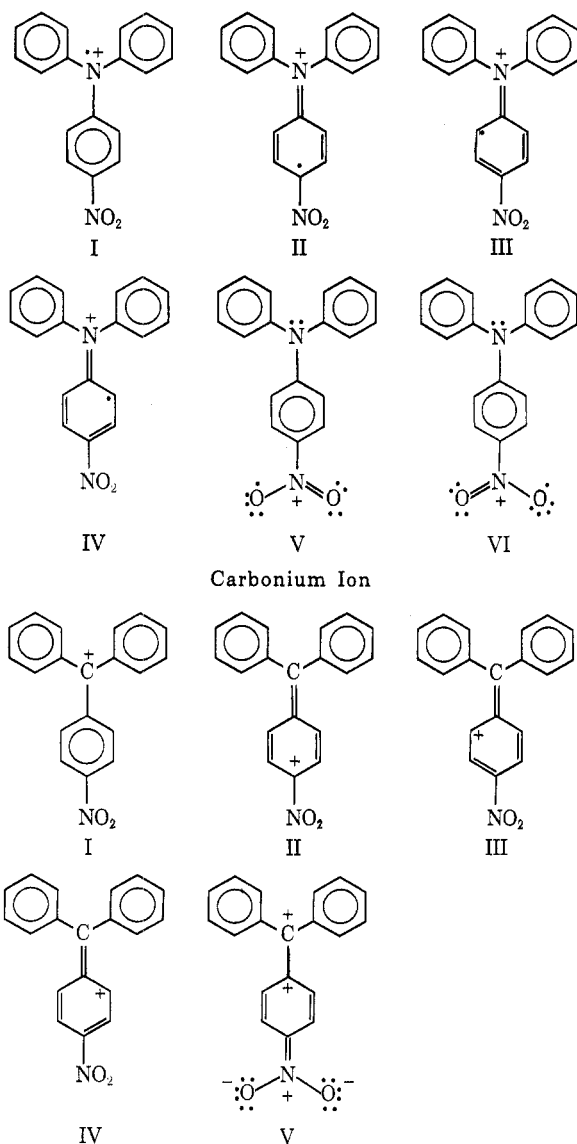squares of the atomic orbital coefficients in the frontier orbital (HFMO). It should be stressed that the

CHART II
RESONANCE FORMS FOR THE 4-NITROTRIPHENYLAMINIUM CATION
RADICAL AND THE 4-NITROTRIPHENYLMETHYL CARBONIUM ION

Cation Radical

Carbonium Ion

numbers above are only valid in a relative sense, but they do confirm the results of the resonance arguments presented previously.

It is interesting to note that a plot of the open para site unpaired electron densities *vs.* the coupling rate constants actually gives a fairly satisfactory linear plot, again with the exception of molecules with strong electron-donating substituents. Thus, such coupling rate data, when correlated with other physicochemical properties such as epr coupling constants, may be useful in deriving new HMO heteroatom parameters for various substituents in cation radicals. Such studies are presently under way for several series of organic cation radicals.

Aside from the strong electron donors, only two other points seem grossly out of line. The formyl derivative, 17, appears to be much less stable than would have been predicted from the σ value of 0.22. The phenyl derivative 9, on the other hand, is more stable than would have been predicted from previous data; this is no doubt due to the increase in the breadth of the π system realized by introduction of an added phenyl group. This added delocalization is verified by simple HMO calculations which show appreciable electron density in the phenyl substituent ring, even with a fairly severe twist angle between it and the adjacent ring. Delocalization of the unpaired electron into a phenyl ring is a "bonus" not to be unexpected in cation radical systems.

Although the data presented here are hardly conclusive, the following corrected σ values for cation radicals ($\sigma \cdot {}^+$?) are suggested with the full realization that they will no doubt be refined and/or corrected in future studies.

R	$\sigma \cdot {}^+$	R	$\sigma \cdot {}^+$
OCH₃	−1.4	OC₆H₅	−1.0
OC₂H₅	−1.35	C₆H₅	−0.4
NHCOCH₃	−1.2	CHO	0.5–0.6

Although the above argument based on resonance stabilization and HMO data for substituents 1–4 seems sound, an alternate possibility would be that the plot in Figure 1 could consist of two linear regions, one composed of substituents 1–4 and the other comprised of the remaining functional groups.[31] This raises the possibility of different mechanisms being operative in the two linear regions; this certainly cannot be excluded at this point. Investigation of alternate mechanisms to the one proposed are being actively pursued by various electrochemical methods. One alternate mechanism is the previously mentioned radical–parent reaction, which might be occurring for compounds 1–4 due to the enhanced radical stability, thus allowing time for diffusion away from the electrode out into solution where collision with parent molecules is more likely.

Another possibility is that the dimerization step (eq 2 in Scheme I) is actually composed of two processes (this is almost certainly the case) with two attendant rate constants

$$2 \text{ cation radicals} \xrightarrow{k_1} \text{dimer dication} \xrightarrow{k_2} \text{benzidine} + 2\text{H}^+$$
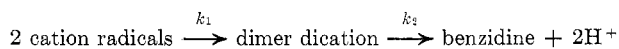
It has been assumed that k_1 is the rate-determining step in all these systems and that the proton loss (k_2) is rela-

(31) This possibility was suggested by a referee.

tively rapid in all cases; it is possible that for some substituents (1–4?) the k_2 step is, in fact, rate determining. This alternative is being investigated by taking measurements of the coupling rates for 4-methoxy- and 4-methyltriphenylamine and the corresponding para-deuterated analogs. If proton loss is rate determining in these systems, then a primary isotope effect should be seen.

These mechanistic alternatives are being explored more fully, but it is felt that the radical–radical pathway is operative in these amine systems and that resonance stabilization through electron delocalization will require different substituent parameters from those for carbonium ions in some cases.

In summary, then, it appears that cation radical stabilities are fairly well predicted by existing σ^+ values in the literature, with the exception of the formyl, phenyl, and strong electron-donating substituents. Studies now in progress on the coupling rates of electrochemically generated carbazole cation radicals, as well as spectroscopic studies on several aromatic amine cation radical systems, should yield a reliable set of reactivity parameters to describe the effects of different functional groups upon cation radical stabilities.

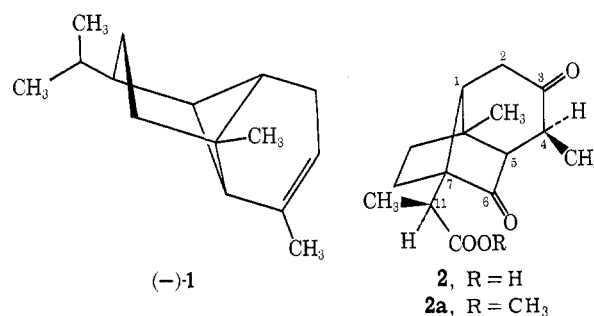---

Chemistry of Santonic Acid. Oxidative and Reductive Modifications[1,2]

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Reduction of santonic acid (2) with Na/Hg in aqueous base gives the previously reported "dihydrosantonic acid" which is now shown to be 4. The C-11 epimer of 4 (*i.e.*, 6) is similarly obtained from metasantonic acid (5), and is also found to be formed by epimerization of 4 during prolonged reductions of 2. An acetoxy lactone (mp 204°) previously reported to be obtained on treatment of "dihydrosantonic acid" with acetic anhydride is shown to be 8 and was probably derived from 6 present as a contaminant in earlier preparations of 4; a new acetoxy lactone, 7 (mp 140°), was obtained from pure 4. An attempt to prepare "dihydrosantonide" by heating 4 in acetic acid at 145–150° gave 10. Reduction of 2 with NaBH₄ gave 11. Methyl ester 11a gave mesylate 13a with CH₃SO₂Cl and acetate 13b with acetic anhydride–HClO₄. Mesylate 13a on acetolysis (acetic acid, sodium acetate) gave epoxy acetoxy ester 14, as evidenced by formation of 11 on hydrolysis. Heating either 11 with CH₃OH–H₂SO₄ or 13a with collidine gave olefins 15 and 16a. The presence of a dissymmetric β,γ-unsaturated ketone chromophore in 16a gives rise to a very strong negative Cotton effect in the ORD and CD curves of 16a which is of the magnitude observed for some other ketones of this type. Lithium–ammonia reduction of 17 yielded 18, which gave 6β alcohol 3 on deketalization; similarly, Li–NH₃ reduction of 16 gave 19. Reduction of 17 with LiAlH₄ afforded 20 and 21. Treatment of 20 with HCl gave lactone 22, which afforded 6α alcohol 23 on basic hydrolysis. Treatment of the mesylate of 18a (24) with potassium *tert*-butoxide yielded sultone 25, which gave 26 on hydrolysis. Deketalization of 24 afforded 3-keto mesylate 27, which gave 28 on contact with Al₂O₃. Alkaline peroxide oxidation of 2 gave "aposantonic acid" (29), for which a stereostructure is proposed; a previously unreported keto lactone acid (31) formed by Baeyer–Villiger oxidation of 2 was also obtained. Repetition of the previously reported hypobromite oxidation of 2 gave "oxysantonic acid," now formulated as 32 on the basis of analytical and spectroscopic data for several formerly reported derivatives of 32.

The assignment of a tricyclo[4.4.0.0²,⁷]decane structure to (−)-copaene (1)[3] and related naturally occurring sesquiterpenoids[4] has stimulated interest in the synthesis of this system.[5] In an attempt to achieve a synthesis of (+)-1 *via* the route outlined in Scheme I, santonic acid (2)[6,7] was utilized as starting material for the preparation of suitable derivatives of 3. Although

(−)-1   2, R = H
                         2a, R = CH₃

an example of the key 5 → 4 ring contraction step[8] has not been effected to date, the work described in this report has led to clarification of several previously reported transformations of santonic acid (2). These are discussed along with several additional reactions of 2 and related derivatives.

Reduction of Santonic Acid. A. Sodium Amalgam

(1) Abstracted from the Ph.D. Dissertation of D. S. Daniel, Washington University, 1970.

(2) A portion of this work has been outlined in a preliminary communication: A. G. Hortmann and D. S. Daniel, *Tetrahedron Lett.*, 2599 (1970).

(3) (a) G. Büchi, S. H. Feairheller, P. De Mayo, and R. E. Williams, *Proc. Chem. Soc.*, 214 (1963); *Tetrahedron*, **21**, 619 (1965); (b) V. H. Kapadia, B. A. Nagasampagi, V. G. Naik, and S. Dev, *Tetrahedron Lett.*, 1933 (1963); *Tetrahedron*, **21**, 607 (1965).

(4) *E.g.*, ylangene, O. Motl, V. Herout, and F. Sorm, *Tetrahedron Lett.*, 451 (1965); copadiene, V. H. Kapadia, V. G. Naik, M. S. Wadia, and S. Dev, *Tetrahedron Lett.*, 4661 (1967); mustakone, ref 3b.

(5) A synthesis of (±)-copaene and (±)-ylangene has been described: C. H. Heathcock, R. A. Badger, and J. W. Patterson, Jr., *J. Amer. Chem. Soc.*, **89**, 4133 (1967).

(6) R. B. Woodward, F. J. Brutschy, and H. Baer, *ibid.*, **70**, 4216 (1948).

(7) For a review of santonic acid chemistry, see J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge University Press, New York, N. Y., 1952, pp 295–311. The stereochemistry at C-11 in santonin has since been shown to be 11*S*: J. D. M. Asher and G. A. Sim, *Proc. Chem. Soc.*, 335 (1962), and references cited therein.

(8) To our knowledge, the key ring-contraction step depicted in Scheme I has no precedent. Conceptually it may be viewed as analogous to the pinacol-type rearrangements observed for oxyanions derived from 1,2-diol monosulfonate esters. For a review, see D. Redmore and C. D. Gutsche, *Advan. Alicycl. Chem.*, **3**, 46 (1971).