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Rate Constants for Some Electrophilic Reactions of Benzyl, Benzhydryl, and Trityl Cations in Solution[1]

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Abstract: Absolute rate constants have been determined by the pulse radiolysis technique for several electrophilic reactions of the benzyl, the benzhydryl, and the trityl cation in 1,2-dichloroethane solution. The rate constants for the reactions of these carbonium ions with chloride ion, with bromide ion, and with iodide ion are all very nearly the same, namely 6×10^{10} M^{-1} s^{-1} at 24 °C. The values very likely represent the diffusion controlled limit for the ion combination reactions. The rate constants for the reactions with triethylamine, tri-*n*-propylamine, and tri-*n*-butylamine range from 2.0×10^9 to 7×10^6 M^{-1} s^{-1} at 24 °C. With increasing phenyl substitution, the decreasing trend in the magnitude of the rate constant is consistent with the combined electronic and steric effects. With increasing size of the amine, the decrease in the value of the rate constant seems to indicate that the steric effect predominates. The values of the rate constants for reactions of benzyl and of benzhydryl cation with methanol, ethanol, and 2-propanol indicate the following. The rate constant is higher for reaction with the alcohol dimer in solution than with alcohol monomer. The rate constants for reaction with alcohol monomer have values of 1×10^8 M^{-1} s^{-1} or lower.

We have shown in a recent report[2] that reactive arylcarbenium ions can be formed in solution and observed on a submicrosecond time scale by the pulse radiolysis method.[3] With this fast reaction method, the absolute reactivity of these carbonium[4] ions may be determined for a variety of their reactions. The optical absorption spectrum of the benzyl cation, which had not been observed by other methods, was thus determined,[2] and absolute rate constants for a few commonly known types of reactions were obtained.

These investigations have now been extended to a systematic determination of the rate constants, in 1,2-dichloroethane solution, of several electrophilic reactions of three arylcarbenium ions, namely benzyl cation, $C_6H_5CH_2^+$, benzhydryl cation, $(C_6H_5)_2CH^+$, and trityl cation, $(C_6H_5)_3C^+$. The nucleophiles for which the reactivity was determined are halide ions, tertiary aliphatic amines, and some aliphatic alcohols. Rate constants ranging from 7×10^6 to 8×10^{10} M^{-1} s^{-1} at 24 °C were obtained.

Experimental Section

As in our earlier studies,[5] the source of the electron pulse was a Varian V-7715A electron linear accelerator delivering 3–4 MeV electrons in pulses ranging from 20 to 1500 ns duration. Pulse current was about 300 mA for pulse duration of 100 to 1500 ns and about 600 mA for pulse duration of 80 ns or less. Electron pulses ranging from 40 to 800 ns were used in this work. Transient absorption spectra were determined using an RCA 1P28 or RCA 7200 photomultiplier as detector. The time resolution of the detection system was about 5 ns with the 1P28, so that it was feasible to observe the kinetics on a submicrosecond time scale. A Bausch and Lomb grating monochromator, type 33-86-25, *f*/3.5, with a grating having a dispersion factor of 7.4 nm/mm was used. Exit slit widths were always 0.4 mm or less, resulting in a band-pass of 3 nm or less. Appropriate Corning filters were used to eliminate second-order components from the analyzing light beam.

Our standard 20-mm reaction cells, equipped with high-purity silica windows, were used in all experiments with, for the most part, a double pass of the analyzing light beam. A full description of the optical arrangement and the electronic detection system has been provided.[3b,5] All the data were accumulated at 24 ± 1 °C.

The solvent used exclusively was 1,2-dichloroethane (1,2-DCE), reagent grade, from Matheson Coleman and Bell. It was purified by a scheme detailed elsewhere.[6] Just prior to each experiment, the desired quantity of 1,2-DCE was distilled in vacuo into the reaction cells from a storage bulb, and the amount distilled was determined by weight difference.

A variety of compounds was used as carbonium ion precursors: dibenzylmercury from Alfa Inorganics; bromodiphenylmethane, technical grade, from Chemical Samples Co.; chlorodiphenylmethane, technical grade, from Chemical Samples Co.; triphenylmethanol from Aldrich Chemical; and triphenylmethyl bromide from J. T. Baker and Co. Dibenzylmercury was recrystallized from absolute ethanol and stored in the dark until used. Chlorodiphenylmethane was purified by a series of fractional freezing cycles, followed by treatment with activated charcoal. It was then dried with barium oxide and stored in a closed vessel until used. In some experiments involving bromodiphenylmethane, the compound was used as obtained. Otherwise it was purified by vacuum sublimation, which resulted in only a slight increase in the lifetime of the benzhydryl cation in the DCE solution. Triphenylmethanol was recrystallized from absolute ethanol, the filtrate being treated with activated charcoal. Triphenylmethyl bromide was recrystallized from DCE.

Additionally, the following compounds were used as reactants in determining absolute rate constants: tetraethylammonium bromide and tetraethylammonium iodide from ICN-K&K Laboratories, triethylamine from J. T. Baker Chemical Co., tri-*n*-propylamine from two sources, Aldrich Chemical Co. or ICN-K&K Laboratories, tri-*n*-butylamine from Matheson Coleman and Bell as well as from ICN-K&K, methanol from Eastman, ethanol from U.S.I., and 2-propanol from Matheson Coleman and Bell.

The quaternary ammonium salts were used as obtained. The triethylamine was purified by distillation under argon into lithium alu-

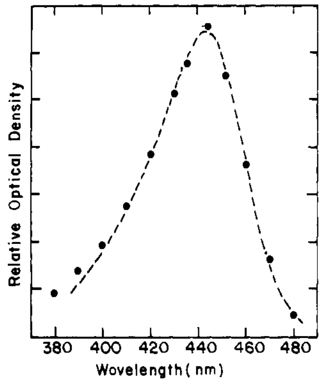

Figure 1. Optical absorption spectrum of the benzhydryl cation in 1,2-DCE solution containing 10^{-2} M benzhydryl bromide as the precursor of the carbonium ion. The spectrum is shown at the end of a 600-ns electron pulse. The dashed line is from the literature (ref 10) where the spectrum was obtained in concentrated sulfuric acid solution.

minum hydride, followed by distillation onto a freshly prepared potassium mirror in vacuo. After contacting the potassium mirror for several days, the solution was thoroughly degassed by repeated freezing-evacuating-thawing cycles. It was then distilled onto another freshly prepared potassium mirror for storage. Both the tri-*n*-propylamine and the tri-*n*-butylamine were purified using the following standard technique.[7] The amine was dissolved in aqueous sulfuric acid, and the pH was adjusted to 4 or lower. The solution was then extracted with ethyl ether, and the ethereal layer was discarded. The resulting aqueous phase was made alkaline by the addition of a concentrated sodium hydroxide solution. The resultant biphasic mixture was separated to give the amine, which was subsequently dried with barium oxide and fractionally distilled under argon into storage. The alcohols were purified by distillation in vacuo to a bulb containing a freshly prepared sodium mirror. The resulting sodium alkoxide solutions were degassed and distilled twice in vacuo into small storage bulbs.

In cases where the compounds used in a run had an appreciable vapor pressure, the desired quantity was distilled in vacuo from a storage bulb, and the amount was determined by weight difference. Compounds having negligible vapor pressure were transferred in known quantities by pipetting into the reaction cells just prior to the experiment. Except for those cases noted, all manipulations, preparations, and measurements were carried out under high vacuum conditions.

Results and Discussion

We have shown in the earlier work[2] on benzyl cation and trityl cation that the pulse radiolysis of solutions of appropriate precursor compounds in 1,2-dichloroethane results in the formation of these carbonium ions. The trityl cation was identified[2] from its observed spectrum[8,9] with peaks at 415 and 439 nm. The spectrum of benzyl cation, with absorption maximum at 363 nm, was identified from the observation that a single common absorption spectrum was obtained[2] from a series of diverse benzyl precursor compounds. In the present work, the benzhydryl cation, formed from the pulse radiolysis of bromodiphenylmethane in 1,2-DCE, was identified from the observation of its known spectrum,[10] shown in Figure 1, with absorption maximum at 454 nm. It is noteworthy that the arylcarbenium ions and carbanions, which may have similar absorption spectra, as in the case of benzyl cation and benzyl carbanion,[11] differ in their reactivity toward molecular oxygen. The carbanion is highly reactive toward oxygen; the carbonium ion does not react with oxygen.

Thus, these three arylcarbenium ions are generated in a process which involves a cationic species of the solvent (DCE^+), formed in the radiolysis, as the primary oxidizing species. The solvent cation species may very likely be the cation radical, but it has not been identified, and there is no basis for ruling out a carbonium ion species from the solvent as the precursor of the arylcarbenium ion. In any event, if the ionization of the aromatic solute, by electron transfer to the solute cation, is *dissociative*, the respective carbonium ions are formed:

$$DCE^+ + Ph_aCH_{(3-a)}X = Ph_aCH_{(3-a)}{}^+ + X\cdot + DCE \quad (1)$$

X may represent halogen atom, hydroxyl group, or, as in the case of mercury or sulfur compounds,[2] an organo-mercury or organo-sulfur group, and a may have the value 1, 2, or 3. With sufficiently high concentration of the precursor compound (2×10^{-3} to 0.1 M), the formation of the carbonium ion is essentially complete at the end of the pulse, and no formation with a half-life in excess of 10 ns is observed. The concentration of precursor which has been used in each case does, of course, depend on the rate constant k_1. In the investigation of the various electrophilic reactions of these arylcarbenium ions, the following precursor compounds were used: benzyl cation was formed from dibenzylmercury, benzhydryl cation from bromodiphenylmethane, and trityl cation from triphenylmethanol.

The rate constants for the electrophilic reactions

$$Ph_aCH_{(3-a)}{}^+ + B \rightarrow \text{products} \quad (2)$$

were determined from the rate curves for the decay of the carbonium ion in the presence of reactant B under the condition $[B]/[Ph_aCH_{(3-a)}{}^+] > 100$, so that the reaction is pseudo first order. In most of the reactions studied, the rate of decay of carbonium ion is at least tenfold slower in the absence of B than in its presence. This lifetime in the absence of B is determined largely by the rate of recombination of the carbonium ion with the counterion in the system, likely Cl^-, formed[2] from the DCE in a dissociative electron attachment. Under our pulse conditions, the lifetimes of the various carbocations in the absence of B are roughly 2, 7, and roughly 10 μs for the benzyl, benzhydryl, and trityl cations, respectively. The rate curves for reaction 2 are analyzed in most cases by plotting log optical density vs. time, which gives a straight line, from the slope of which $k_2[B]$ is determined. In the case of the slower reactions with trityl cation, this simple linearization was not feasible, and $k_2[B]$ was determined using an analog computer treatment.

Reactions with Halide Ions. The rate constants for the reaction of the carbonium ions with bromide ion and with iodide ion

$$Ph_aCH_{(3-a)}{}^+ + Br^- = Ph_aCH_{(3-a)}Br \quad (3)$$

were determined in solution containing a sufficient concentration of quaternary ammonium salt to bring the concentration[2] of halide into the range 3×10^{-5} to 3×10^{-4} M. These concentrations were calculated from the ion dissociation constants for the respective salts in DCE which we had determined earlier[2] from conductivity measurements. For each reaction, the rate curve was found linear for a plot of ln D_t vs. t. The pseudo-first-order constants obtained from the slopes of these lines were plotted against concentration of halide ion to determine the bimolecular rate constant. Two examples for benzhydryl and trityl cation with iodide are shown in Figure 2. The rate constants obtained are given in Table I. The uncertainty in the rate constants determined in this way was approximately ±15%.

In the case of the reaction of trityl cation with chloride ion, the rate constant was obtained in a different manner. For a solution of triphenylmethanol of concentration similar to that in the other experiments with trityl cation, in the absence of any other reactant, the decay rate of the trityl cation was found to fit a second-order rate law. This is consistent with our interpretation that this natural decay consists of reaction with the solvent ion Cl^-. The rate constant for this reaction is obtained from the slope of the second-order plot and the known extinction coefficient for trityl cation,[12] namely $\epsilon = 3.98 \times 10^4$ M^{-1} cm^{-1}. The rate constant for the reaction of trityl cation

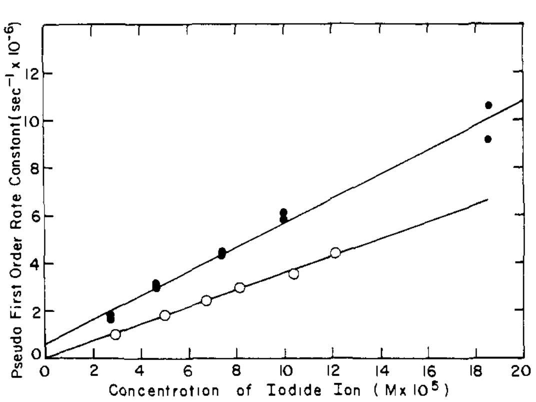

Figure 2. Plot of the pseudo-first-order rate constant for the reactions of carbonium ions with iodide ion in 1,2-DCE at 24 °C: (●) benzhydryl cation with iodide ion; (○) trityl cation with iodide ion. The rate constants are 5.2 × 10^{10} M^{-1} s^{-1} and 3.6 × 10^{10} M^{-1} s^{-1}, respectively.

Table I. Rate Constants for the Reaction of Arylcarbenium Ions with Halide Ions in DCE (Units Are M^{-1} s^{-1} × 10^{-10})

	I^-	Br^-	Cl^-
$PhCH_2^+$	4.9 ± 0.5	5.2 ± 0.6	
Ph_2CH^+	5.2 ± 0.6	7.0 ± 1.0	
Ph_3C^+	3.6 ± 0.5	5.6 ± 0.7	8.0 ± 2.5

with chloride ion is (8.0 ± 2.5) × 10^{10} M^{-1} s^{-1}, very similar to the values for the other carbonium ion combination reactions obtained by a different method.

These values, which are very nearly the same for the three arylcarbenium ions, seem to show a small trend with halide ion. The values likely represent the diffusion-controlled limiting rate constants for the particular ion combination reactions. The small increase is in the direction of increasing mobility of the anion, which in turn has an inverse dependence upon the ionic radius. The effect of the radius factor is, however, partly cancelled since it appears in the Smoluchowski equation as a parameter in both the interaction cross section and in the diffusion coefficient.

Reactions with Tertiary Alkyl Amines. Three tertiary alkyl amines were selected as reactants in order to examine the magnitude of steric effects in these electrophilic reactions. For the reactions of benzyl cation with triethyl, tri-*n*-propyl, and tri-*n*-butylamine, and for benzhydryl cation with these three amines, first-order decay curves were observed. The concentration ranges of amine, over which the first-order plots were obtained, were 1-9 mM for reactions with benzyl cation and 2-15 mM for reactions with benzhydryl cation. With trityl cation, for which the rate constants were evaluated by a curve-fitting procedure (vide infra), the range covered was 0.2-1.6 mM for triethylamine, 0.8-3.6 mM for tri-*n*-propylamine, and 7-45 mM for tri-*n*-butylamine. Two examples of the plot of pseudo-first-order constant against concentration, from which the rate constants in Table II were obtained, are shown in Figure 3. The uncertainty in these rate constants is approximately ±15%. For the reactions of trityl cation (for which the rate constants have declined to values of 10^8 or lower) several complications are encountered. Firstly, the higher amine concentration necessary for the reaction to be observed over a convenient time interval results in a decrease in the concentration ratio of triphenylmethanol to amine, with the amine competing successfully for DCE^+. This results in a somewhat lower yield of the trityl cation. A more important consequence of this competition by the amine for DCE^+, which represents a problem particularly in the case of trityl cation, is that the amine itself forms an absorbing transient with a spectrum which overlaps with that of the trityl cation at the wavelength of observation. This state of affairs, which is more acute with triethylamine and tripropylamine, restricts the range of amine concentration which may be investigated for a particular concentration of the carbonium ion precursor. As a result, the rate constants for such cases may have a somewhat larger experimental uncertainty.

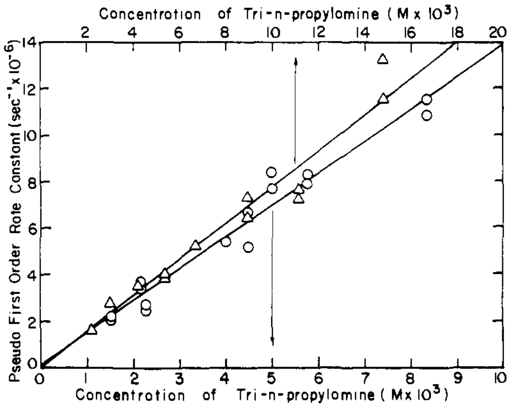

Figure 3. Plot of the pseudo-first-order rate constant for the reactions of benzyl cation and of benzhydryl cation with tri-*n*-propylamine in 1,2-DCE at 24 °C. The abscissa for benzyl cation (○) is shown at the bottom; that for benzhydryl cation (△) at the top. The rate constants are 1.4 × 10^9 and 7.7 × 10^8 M^{-1} s^{-1}, respectively.

Table II. Rate Constants for the Reactions of Arylcarbenium Ions with Tertiary Alkyl Amines in DCE (M^{-1} s^{-1})

	$(C_2H_5)_3N$	$(C_3H_7)_3N$	$(C_4H_9)_3N$
$PhCH_2^+$	(2.0 ± 0.3) × 10^9	(1.4 ± 0.3) × 10^9	(1.0 ± 0.2) × 10^9
Ph_2CH^+	(1.2 ± 0.2) × 10^9	(7.7 ± 0.5) × 10^8	(5.4 ± 1.0) × 10^8
Ph_3C^+	(1.3 ± 0.5) × 10^8	(1.3 ± 0.5) × 10^8	(7.0 ± 3.0) × 10^6

For the reactions with rate constants of 10^8 M^{-1} s^{-1} or lower, there is a complication in the kinetics which calls for an interpretation of the rate curves by other than the standard linearization methods generally applicable. For these reactions, the specific rate of the reverse reaction is not negligible; for the reaction of trityl cation with tributylamine, the reverse rate constant is approximately 4 × 10^4 s^{-1}. Accordingly, the pseudo-first-order rate constants in these cases were obtained not from first-order plots but from a curve-fitting procedure utilizing a Systron Donner, SD 40/80 analog computer, in which the reverse reaction, as well as the reaction with the solvent counterion, was taken into account. Such a curve-fitting result is shown in Figure 4 for tributylamine. The resulting plot of the pseudo-first-order constant against amine concentration, from which the rate constant is determined, is shown in Figure 5. The rate constants obtained by this procedure involving a smaller range of amine concentration, have a somewhat greater uncertainty, amounting to about ±40%, as may be seen in Table II.

The rate constants in this table show a clear, fairly smooth trend. They show a decrease in magnitude with increasing phenyl substitution of the carbenium ion, with the decrease amounting to a factor of 1.8 in going from phenylcarbenium to diphenylcarbenium ion and roughly an order of magnitude in going from diphenylcarbenium to triphenylcarbenium ion. This trend is to be expected as a result of both the electronic effect (increased charge delocalization with increased degree of phenyl substitution) and the steric effect. It is perhaps surprising that both factors together produce as small an effect as is observed. The rate constants also decrease, but to a lesser extent, with increase in size of the alkyl group in the trialkyl amines. Here it would seem that the steric effect is dominant over the opposite electronic effect of electron donation by the alkyl group.

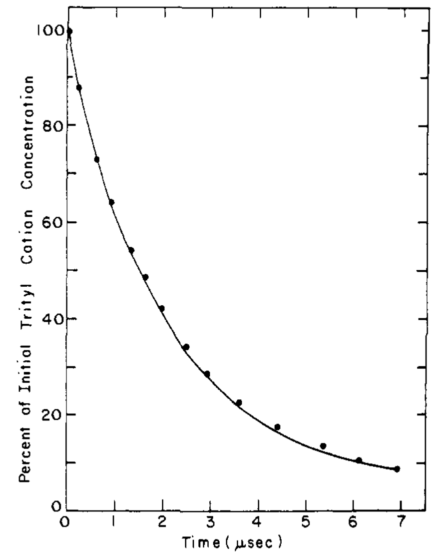

Figure 4. A rate curve for decay of trityl cation in reaction with tributylamine in 1,2-DCE at 24 °C. The points are taken from the observed rate curve. The solid line is a computer simulation of the decay process. A pseudo-first-order rate constant is obtained from this simulation and is plotted in Figure 5.

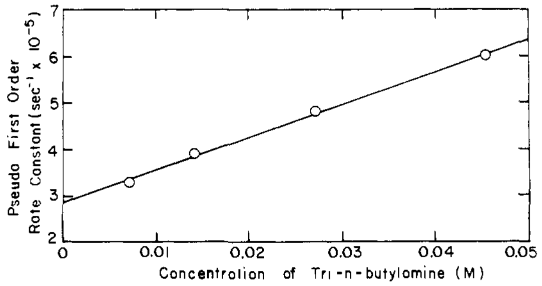

Figure 5. Plot of the pseudo-first-order rate constants for the reaction of trityl cation with tributylamine in 1,2-DCE at 24 °C, obtained from analog computer simulations. The rate constant for the reaction is 7.0 × 10^6 M^{-1} s^{-1}.

Reactions with Aliphatic Alcohols. With the extension of these investigations to benzhydryl cation, rate constants have now been determined for the reactions of benzyl cation with methanol and ethanol and of benzhydryl cation with methanol, ethanol, and 2-propanol. In the earlier work on benzyl cation,[2] rate constants of 7.4 × 10^7 and 1.3 × 10^8 M^{-1} s^{-1} were reported for methanol and ethanol, respectively. In extending the determination to benzhydryl cation, the following interesting complication in the kinetics was encountered. The individual rate curves for cation decay, as in the case of benzyl cation, followed a first-order rate law over the entire range of alcohol concentration used, namely 1-6 × 10^{-2} M. However, the plot of the pseudo-first-order constants against alcohol concentration was found to deviate significantly from linearity for methanol and ethanol as shown in Figure 6. A linearization of the data is obtained on the basis of the following interpretation. There is substantial independent evidence,[13,14] that at sufficiently high concentration these alcohols are present not only in monomeric form, but also in higher aggregates. The deviation from linearity in Figure 6 may be understood in these terms if it is assumed that the reactivity of the carbonium ion is slower with the alcohol monomer than with the higher aggregate. Szwarc[15] has encountered a similar phenomenon in the case of protonation reactions of aromatic radical anions in dimethoxyethane and has treated the data by the assumption that only alcohol monomers and dimers are present at equilibrium, or at any rate are kinetically significant:

$$2\mathrm{ROH} \overset{K_e}{=} (\mathrm{ROH})_2 \qquad (4)$$

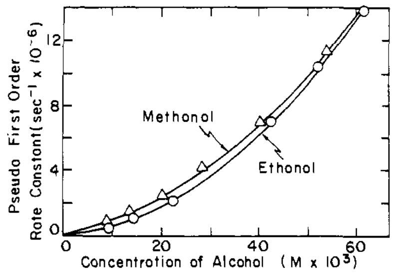

Figure 6. Plot of the pseudo-first-order rate constants for the reactions of benzhydryl cation with methanol (△) and with ethanol (○) in 1,2-DCE at 24 °C against concentration of the alcohol.

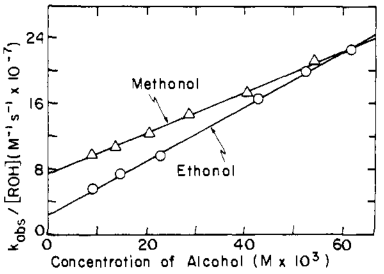

Figure 7. Plot of k_{obsd}/[ROH] vs. [ROH] for the reactions of benzhydryl cation with methanol (△) and with ethanol (○) in 1,2-DCE at 24 °C.

Table III. Rate Constants for the Reaction of Arylcarbenium Ions with Aliphatic Alcohols

	k_m (M^{-1} s^{-1} × 10^{-7})	$K_e k_d$ (M^{-2} s^{-1} × 10^{-8})
Ph_2CH^+ + methanol	8	30
Ph_2CH^+ + ethanol	2	30
Ph_2CH^+ + 2-propanol	10	5
$PhCH_2^+$ + methanol	6	2
$PhCH_2^+$ + ethanol	10	

The differential rate equation for the decay of carbonium ion is:

$$\frac{-d[\mathrm{Ph_2CH^+}]}{dt} = k_m[\mathrm{ROH}][\mathrm{Ph_2CH^+}] + k_d[(\mathrm{ROH})_2] \times [\mathrm{Ph_2CH^+}] \qquad (5)$$

where k_m is the rate constant for reaction with the monomer, and k_d is the rate constant for reaction with the dimer. This gives:

$$\frac{-d[\mathrm{Ph_2CH^+}]}{dt} = (k_m[\mathrm{ROH}] + k_dK_e[\mathrm{ROH}]^2)[\mathrm{Ph_2CH^+}] \qquad (6)$$

where the term in parentheses has a constant value, under condition of excess alcohol, and is equivalent to the observed first-order rate constant, k_{obsd}, for the cation decay. A plot of k_{obsd}/[ROH] vs. [ROH] should then give a straight line with slope k_dK_e and intercept k_m. It is assumed that the degree of dimerization is sufficiently small so that the monomer concentration may be represented, to a first approximation, by the alcohol concentration. Such a plot of the data for the reaction of benzhydryl with methanol and ethanol is shown in Figure 7, which gives the data shown in Table III. The excellent linearity obtained supports the validity of the approximation, namely that $K_e \ll 1$ and, therefore, $k_d/k_m > 10$ for benzhydryl cation. In the case of 2-propanol, the deviation from linearity of the plot of pseudo-first-order rate constants against concentration is not so great, and rather similar values are obtained from either analytical treatment. The value in Table III is obtained from the plot of eq 6.

Similar data for the reaction of benzyl cation with methanol, over a concentration range of 4-60 mM, show only a small degree of curvature and, when subjected to the foregoing treatment, give a value of $(6 \pm 1.5) \times 10^7\ M^{-1}\ s^{-1}$. This is slightly lower than the previous value[2] of 7.4×10^7, but not in disagreement. The value for benzyl cation and ethanol is taken from the previous paper[2] since the very small deviation from linearity did not seem to call for the more complex interpretation. The uncertainty in the values of k_m is approximately ±20%, in $K_e k_d$ approximately ±25%. The values for k_m indicate no obvious trend in the alcohol series.

The higher reactivity of the arylcarbenium ion toward alcohol dimer than toward monomer is interesting but may not be readily predictable on any simple basis involving either higher electron density on the oxygen in the dimer, or a lower charge repulsion toward the reacting carbonium ion. The product of the reaction is an ether,[16] and it is interesting to note that the leaving group from the protonated ether intermediate formed from the monomer is a proton, while for that formed from the dimer is the alkoxonium ion, a bonded, stabilized state of the proton.

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Radical Additions to Di-*tert*-butylsulfur Diimide and Di-*tert*-butylcarbodiimide[1]

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Abstract: A variety of transient radicals, $R_nM\cdot$, add to di-*tert*-butylsulfur diimide to give a new class of nitrogen-centered radicals, *N*-aminothiyl-*N*-alkylamino radicals, $Me_3C\dot{N}SN(CMe_3)MR_n$. The EPR parameters of these radicals indicate that the unpaired electron is located principally in the $N_\alpha\ 2p_z$ orbital and that the α-*tert*-butyl group, the two nitrogens, and the sulfur lie in, or close to, the nodal plane of this orbital. These radicals decay with first-order kinetics, and some of them are very persistent. Radical addition to di-*tert*-butylcarbodiimide appears to be a less facile process, since only $CF_3O\cdot$ gave a simple adduct, $Me_3CN{=}C(OCF_3)\dot{N}CMe_3$. This 1,3-diazaallyl radical decays with second-order kinetics; $\log (k/M^{-1}\ s^{-1}) = (7 \pm 1) - (2.5 \pm 1.2)/\theta$, where $\theta = 2.3RT$ kcal/mol. Trimethysilyl radicals add to di-*tert*-butylcarbodiimide (and other carbodiimides), but only the extremely persistent $(Me_3Si)_2\dot{C}N(SiMe_3)_2$ radical can be observed.

Very few nitrogen-centered radicals have been prepared by radical additions to a common precursor. More usually, N-centered radicals have been generated from precursors individually synthesized (often with considerable difficulty), such as tetrazenes,[4,5] dialkylaminodialkoxyphosphines,[5,6] alkoxyalkylamines,[7-9] etc., which has made studies of structural effects on EPR spectra and on reactivity slow and tedious. In a continuing search for simple methods for generating N-centered radicals, we found that certain readily prepared transient radicals, $R_nM\cdot$, will add to di-*tert*-butylsulfur diimide to give a new class of radicals, *N*-aminothiyl-*N*-alkylamino radicals (**1**).

$$R_nM\cdot + Me_3CN{=}S{=}NCMe_3 \rightarrow Me_3C\dot{N}SN(CMe_3)MR_n$$

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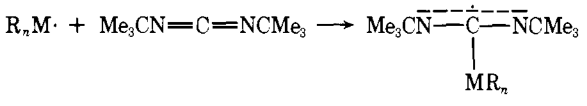
Radical additions to the structurally related di-*tert*-butylcarbodiimide were also explored, but only one member of the desired family of 1,3-diazaallyl radicals could be identified.



$$R_nM\cdot + Me_3CN{=}C{=}NCMe_3 \longrightarrow Me_3C\overline{N}{-}\overset{\cdot}{\underset{\displaystyle MR_n}{C}}{-}\overline{N}CMe_3$$

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Iminoyl radicals,[10] which would be formed by attack at one of the carbodiimide's nitrogen atoms, were never detected.

$$R_nM\cdot + Me_3CN{=}C{=}NCMe_3 \rightarrow Me_3CN{=}\dot{C}N(CMe_3)MR_n$$

Experimental Section

Di-*tert*-butylsulfur diimide[11] and di-*tert*-butylcarbodiimide[12] were prepared by literature methods. All other materials were commercially available samples which were used without further purification. Transient radicals were generated in cyclopropane as solvent directly