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## Reactivity of Arylcarbenium Ions with Alkylamines and Ammonia in Solutions. Kinetic Effect of Cyclopropyl Substitution. Solvent Effect<sup>1</sup>

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**Abstract:** Rate constants have been determined for some selected reactions of arylcarbenium ions with trialkylamines and ammonia in three chlorinated hydrocarbon solvents. They were obtained by pulse radiolysis which permits the direct optical observation of the transient and its reactions in real time. Included among these are the reactions of  $\alpha$ -cyclopropyl- and  $\alpha,\alpha$ -dicyclopropylphenylcarbenium ion. Cyclopropyl substitution is found to produce only a very small kinetic effect. A significant solvent effect is found for only small changes in solvent properties. The results are considered with regard to the relationship between the reactivity of a carbocation and its solvolytic rate.

We have recently reported<sup>2</sup> pulse radiolysis studies of arylcarbenium ions in 1,2-dichloroethane solution in which absolute rate constants for a number of electrophilic reactions of these carbocations were presented. Among these were the reactions with trialkylamines. This work on the amine reactions has been extended to obtain new information on the following: (a) the reactivity of  $\alpha$ -cyclopropylphenylcarbenium ions toward the alkylamines, allowing us to compare our data on the kinetic effect of cyclopropyl substitution with observations from a different type of experiment, namely, with solvolysis data;<sup>3-7</sup> (b) the reactivity in different solvents, which demonstrates that even a small difference in solvent properties can result in a significant change in reactivity of the carbocations; (c) the reactivity of the arylcarbenium ions with ammonia, which will be seen to have a direct bearing on the consideration of mechanism.

### Experimental Section

As previously described,<sup>8,9</sup> the source of the electron pulse was a Varian V-7715A electron linear accelerator, delivering 3-4 MeV electrons at a pulse current of about 300 mA for pulses of 100-1400-ns duration and about 600 mA for pulses of less than 80-ns duration. Electron pulses ranging from 60 to 800 ns were used in this work. The concentration of transients produced was on the order of  $10^{-66}$ - $10^{-7}$  M. All the runs were done at  $24 \pm 1$  °C. Transient absorptions were determined using an RCA 1P28 or RCA 7200 photomultiplier as detector. The time resolution of the detection system is about 5 ns, so

that it was possible to observe the kinetics on a submicrosecond time scale. A Bausch and Lomb grating monochromator, type 33-86-25, f/3.4, was used with grating parameters and exit slit widths such that the band-pass was 3 nm or less. Appropriate Corning filters were used.

Our standard 20-mm reaction cells with high-purity silica windows were used in all experiments. Generally, a double pass of the analyzing light beam was used. A detailed description of the optical arrangement and the detection system has been presented elsewhere.<sup>8,9</sup>

1,2-Dichloroethane (DCE), methylene chloride (MC), and 1,1,2-trichloroethane (TCE) were used as solvents. The DCE was obtained from Matheson Coleman and Bell, the MC from Fisher, and the TCE from Aldrich. The purification has been described.<sup>10</sup> Solvent was transferred into the reaction cell by distillation *in vacuo*, the quantity being determined by weight difference. All liquids were degassed by a series of freeze-evacuation-thaw cycles.

The purification of dibenzylmercury (Alfa Inorganics), bromodiphenylmethane (Chemical Samples Co.), and triphenylmethanol (Aldrich) has been described.<sup>2</sup> Cyclopropylphenylcarbinol and dicyclopropylphenylcarbinol (both from Aldrich) were purified by fractional distillation at about 18 Torr. Triethylamine, tripropylamine, and tri-*n*-butylamine (all from Aldrich) were purified as described previously.<sup>2</sup> The quantity of amine transferred into the reaction cell was determined by weight difference. Ammonia (Matheson) solutions in DCE were made up from amounts of ammonia determined by *P-V* measurement of the gas. The concentration of ammonia in solution was determined from the solubility in DCE (8 mol %) for a cell with 80% liquid volume, and assuming Henry's law; the calculation showed that only 1% of the measured amount of ammonia remained in the gas phase.

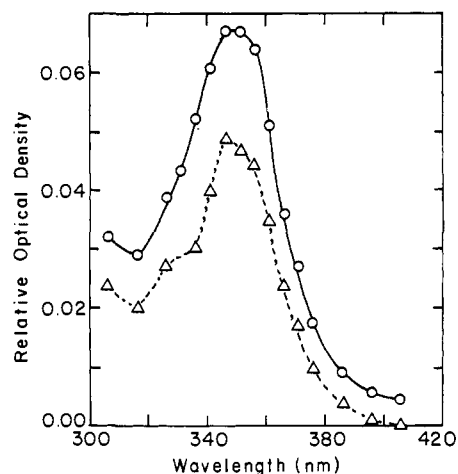
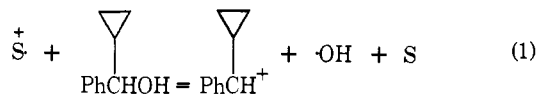


Figure 1. Optical absorption spectrum of the  $\alpha$ -cyclopropylphenylcarbenium ion in 1,2-DCE solution containing  $10^{-3}$  M cyclopropylphenylcarbinol as the precursor to the carbocations. The spectrum is shown 5 (O) and 15  $\mu$ s ( $\Delta$ ) after a 200-ns electron pulse.  $\lambda_{\max} = 347$  nm.

## Results and Discussion

The earlier work,<sup>2,11,12</sup> which had been limited to the benzyl, benzhydryl, and trityl cations in 1,2-dichloroethane solution, has been extended to the investigation of  $\alpha$ -cyclopropyl- and  $\alpha,\alpha$ -dicyclopropylphenylcarbenium ion. In addition, all five of these cations were formed and investigated in methylene chloride, and some data have been obtained in trichloroethane.

**Formation and Identification of the Cations.** As we have pointed out,<sup>2,11,12</sup> the respective cations are formed from various precursor compounds in a dissociative charge transfer involving a solvent cation, for which the overall reaction may be written



Both the  $\alpha$ -cyclopropyl- and the  $\alpha,\alpha$ -dicyclopropylphenylcarbenium ion were formed from the respective carbinols. These two cations were identified from their optical absorption spectra. In the former case a relatively uncomplicated spectrum shown in Figure 1 was obtained, consisting of a UV band with a maximum at 347 nm. This compares with  $\lambda_{\max}$  343 nm reported<sup>13</sup> for the  $\alpha$ -cyclopropylphenylcarbenium ion in strong acid media. As may be seen, this transient band consists of only a single species. The reaction kinetics of this cation were monitored at 345–355 nm.

In the latter case, a more complex absorption spectrum, shown in Figure 2, was obtained from which the cation spectrum was determined by difference. This difference spectrum exhibits two peaks at 296 and 353 nm which compares with peaks at 285, 322, and 340 nm reported<sup>13</sup> for  $\alpha,\alpha$ -dicyclopropylphenylcarbenium ion in strong acid media. To be sure, the overall spectrum seen at  $t = 0$  after the pulse exhibits three peaks at 291, 324, and 351 nm, apparently very similar in detail to the literature.<sup>13</sup> However, this spectrum is complex, and the time-resolved spectra reveal the presence of three transient species. Thus, a short-lived species with a band determined by difference to be at  $\lambda_{\max}$  316 nm decays almost completely within 1  $\mu$ s, and cannot be identified with the cation. There is also seen the growth, over the interval zero to 1  $\mu$ s, of a relatively long-lived species overlapping with the 291-nm band of the cation. In order to obtain the spectrum of the cation, we have simply subtracted the spectrum at 9  $\mu$ s (a time interval over which the cation has nearly completely decayed) from the

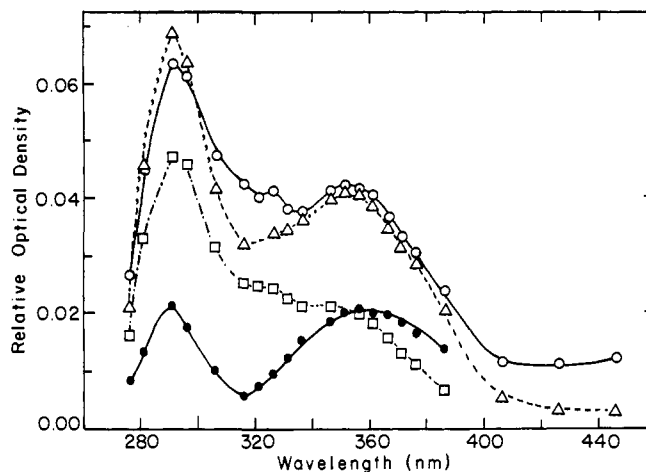





Figure 2. Transient optical absorption spectra obtained following an 80-ns electron pulse in a solution of  $10^{-3}$  M dicyclopropylphenylcarbinol in 1,2-DCE: O,  $t = 0$  after pulse;  $\Delta$ ,  $t = 1$   $\mu$ s after pulse;  $\square$ ,  $t = 9$   $\mu$ s after pulse. The fourth spectrum ( $\bullet$ ) is a difference spectrum obtained by subtraction of the  $t = 9$   $\mu$ s spectrum from the  $t = 1$   $\mu$ s spectrum. This difference spectrum is suggested to be that of the  $\alpha,\alpha$ -dicyclopropylphenylcarbenium ion in 1,2-DCE.

Table I. Rate Constants for Reactions of Arylcarbenium Ions with Alkylamines and Ammonia in DCE at 24 °C ( $M^{-1} s^{-1}$ )

	NH <sub>3</sub>	TEA <sup>a</sup>	TPA <sup>a</sup>	TBA <sup>a</sup>
PhCH <sub>2</sub> <sup>+</sup>	$4.2 \times 10^9$	$2.0 \times 10^9$	$1.4 \times 10^9$	$1.0 \times 10^9$
Ph <sub>2</sub> CH <sup>+</sup>	$4.3 \times 10^9$	$1.2 \times 10^9$	$7.7 \times 10^8$	$5.4 \times 10^8$
Ph <sub>3</sub> C <sup>+</sup>	$2.4 \times 10^7$	$7.3 \times 10^7$	$1.5 \times 10^7$	$4.0 \times 10^6$
 PhCH <sup>+</sup>		$2.2 \times 10^9$	$8.8 \times 10^8$	$3.0 \times 10^8$

<sup>a</sup> The data for benzyl cation and for benzhydryl cation with the three amines are taken from ref 2.

Table II. Rate Constants for Reactions of Arylcarbenium Ions with Alkylamines in MC at 24 °C ( $M^{-1} s^{-1}$ )

	TEA	TPA	TBA
PhCH <sub>2</sub> <sup>+</sup>	$2.8 \times 10^9$	$2.6 \times 10^9$	$2.4 \times 10^9$
Ph <sub>2</sub> CH <sup>+</sup>	$2.9 \times 10^9$	$1.5 \times 10^9$	$1.1 \times 10^9$
Ph <sub>3</sub> C <sup>+</sup>	$1.5 \times 10^8$	$4.5 \times 10^7$	
 PhCH <sup>+</sup>	$2.7 \times 10^9$	$1.7 \times 10^9$	$9.2 \times 10^8$
 PhC- $\triangle^+$	$2.1 \times 10^9$	$1.4 \times 10^9$	

1- $\mu$ s spectrum. The resulting spectrum, shown in Figure 2, has peaks at 296 and 353 nm. The kinetics of reaction of this cation with the alkylamines were observed over the wavelength range 350–375 nm, since the species remaining at 9  $\mu$ s is long lived, and undergoes no significant decay in a submicrosecond interval.

**Absolute Reactivity of the Cations.** Rate constants for the electrophilic reaction of the various arylcarbenium ions with triethyl-, tripropyl-, and tributylamine and with ammonia were determined in 1,2-DCE. These data are shown in Table I. Rate constants for the reaction of all five arylcarbenium ions with the amines were also determined in methylene chloride. These rate constants are shown in Table II.

The rate constants were obtained in the following manner. Since the half-time for the natural decay of the cation in the

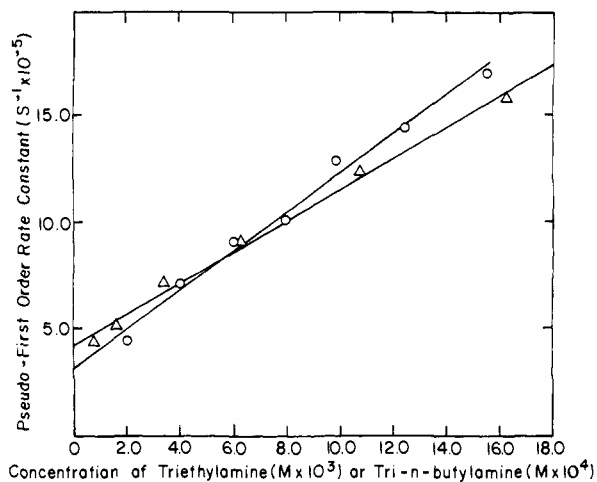


Figure 3. Plot of the pseudo-first-order rate constant for the reactions of the trityl cation with triethylamine in 1,2-DCE ( $\Delta$ ) and of the  $\alpha$ -cyclopropylphenylcarbenium ion with tributylamine in methylene chloride ( $\circ$ ) at 24 °C. The rate constants are  $7.3 \times 10^7$  and  $3.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , respectively.

absence of any added nucleophile ranged from 6 to 20  $\mu\text{s}$ , it was quite feasible to monitor the reaction with the added nucleophile on a submicrosecond time scale. All rate curves were obtained at sufficiently high concentration of the amine so that the reaction was pseudo-first-order. The first-order rate constant was determined from a plot of  $\ln(D_\infty - D_t)$  vs. time, which gave good linearity in all cases. These first-order constants were then plotted against amine concentration, and the rate constants in the tables determined from the slope of the resulting straight line. Figure 3 shows two samples of such a plot, for trityl cation with triethylamine in DCE and for cyclopropylphenylcarbenium ion with tributylamine in MC. The three rate constants for trityl cation with the alkylamines in DCE in Table I are slightly lower than the values reported earlier.<sup>2</sup> They are obtained here in a higher range of amine concentration, permitting their determination from linear plots, with the natural decay negligible, rather than from curve fitting under conditions where the natural decay of the cation was concurrent. The experimental uncertainty is  $\pm 10$ –15% for the values in DCE and about  $\pm 15\%$  for the values in MC.

There are three effects evident in the data in Table I to which we would like to draw attention. The first is the effect of increasing phenyl substitution. If a steric effect and an electronic effect were both operative, each would be expected to contribute to a decrease in the value of the rate constant with increasing phenyl substitution. The data show a large decrease in rate constant only with trisubstitution. The decrease from benzyl to benzhydryl amounts to slightly less than a factor of 2; the decrease from benzhydryl to trityl is much larger, ranging from 16-fold to 130-fold. A similar large decrease is seen in the data in Table II, for MC. This would seem to suggest that the major contribution to the decrease is steric rather than electronic, showing an onset for trityl, and only a small effect upon doubling the number of phenyl groups from benzyl to benzhydryl. We recognize that we are referring, strictly speaking, to gas-phase properties of the molecule.

The second effect is the kinetic effect of cyclopropyl substitution, as evident from the rate constants presented here in both DCE and MC. We may compare our direct determination of reactivity with the concept of "stability" which has its origin either in solvolysis rates or in the heats of formation of the ions. Several workers<sup>3-7,13-17</sup> have commented on the stabilizing effect of the cyclopropyl ring. This was based on the relative ease of formation of  $\alpha$ -cyclopropylcarbenium ions<sup>3-6</sup> and their

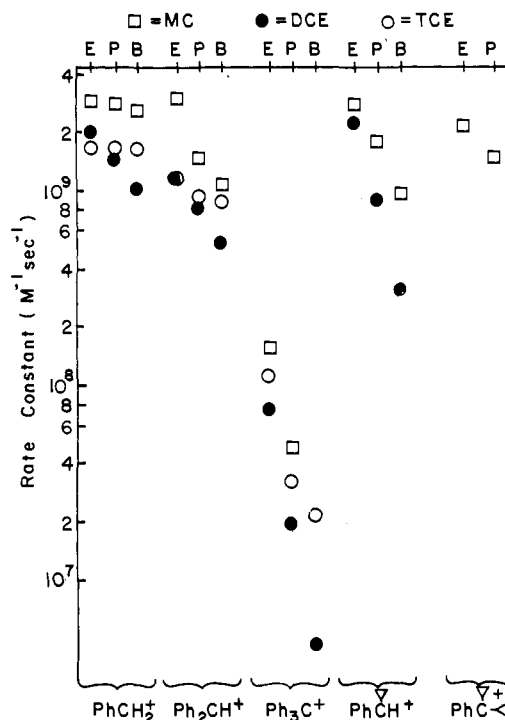
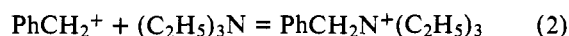


Figure 4. Rate constants (in units of  $\text{M}^{-1} \text{ s}^{-1}$ ) for the reactions of the five arylcarbenium ions (indicated on the abscissa at bottom) with trialkylamines. The data for each cation are presented in separate columns. The values for each nucleophile are identified by the column positions E (triethylamine), P (tripropylamine), and B (tributylamine). The solvents are identified by  $\square$ , methylene chloride,  $\bullet$ , dichloroethane, and  $\circ$ , trichloroethane. Note that the ordinate scale is logarithmic.

resulting rapid solvolytic rates. The stabilization was reported to be greater than that of an allyl group<sup>3-6</sup> or a phenyl ring<sup>14,15</sup> in the carbenium ion. Furthermore, the steric hindrance of the cyclopropyl ring, which is normal to the plane of the carbocation,<sup>18</sup> is thought to be approximately equal to that of a phenyl ring.

Cyclopropyl substitution in the arylcarbenium ions in Tables I and II does not reveal such an effect on the reactivity. In DCE, the reactivity of  $\alpha$ -cyclopropylphenylcarbenium ion may be described as follows: toward TEA it is equal to that of benzyl and twice that of benzhydryl; toward TPA it is slightly higher than that of benzhydryl; toward TBA it is somewhat less than that of benzhydryl. It should be pointed out that a rate constant of  $2 \times 10^9$  is about threefold lower than the diffusion-controlled limit. In MC, the effect of cyclopropyl substitution is either negligible or very small, except at the trisubstituted stage where there is a large difference between phenyl and cyclopropyl. It is clear also that there is a solvent effect.

The third effect to be seen in Table I, which is pertinent to the consideration of mechanism, is concerned with the reactivity toward ammonia. The reactivity with ammonia shows a decrease of more than two orders of magnitude from benzhydryl to trityl. Again this may be due mainly to the steric effect. But note that the trityl rate constant is threefold lower for ammonia ( $2.4 \times 10^7$ ) than it is for TEA ( $7.3 \times 10^7$ ). This difference between ammonia and TEA cannot be due to a steric effect, which clearly should result in a lower rate constant for TEA than for ammonia. We suggest that the following consideration of mechanism may explain the foregoing result. The general electrophilic reaction with the amines is, presumably, the formation of a quaternary ammonium ion:



This is not the only reaction possible; electron transfer may

occur, depending upon the relative magnitude of the rate constants for electron transfer and for the reaction of type 2. For the trityl cation, the rate constant for quaternary ammonium ion formation is sufficiently reduced by the steric effect so that electron transfer may become competitive. Electron transfer is possible for TEA since its ionization potential<sup>19</sup> is only 7.50 eV. Ammonia, on the other hand, has a much higher ionization potential,<sup>19</sup> namely, 10.15 eV, and the electron transfer is far less likely to occur. Hence, we have the reaction of type 2, with a lower rate constant for NH<sub>3</sub>.

Another kinetic effect is evident from the data in the two tables, as well as from data for TCE. There is a significant solvent effect. In MC, the trend in the rate constants for the benzyl cation with the amines is virtually eliminated. There is also a solvent dependence in the ratio  $k_{\text{benzyl}}/k_{\text{benzhydryl}}$ , which is 1.8 in DCE, the same for all three amines, but which varies from 1.0 to 2.4 in MC. In TCE, the rate constants for benzyl with both TEA and TPA are  $1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , and for benzhydryl with TEA and with TPA are respectively  $1.2 \times 10^9$  and  $8.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .

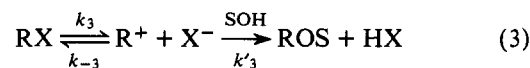
What seems remarkable about the solvent effect is that the properties of the solvents are so similar. DCE and MC exhibit no significant difference in dielectric constant, density, enthalpy of vaporization, and nucleophilicity. The viscosities, dipole moments, and polarizabilities are different. The viscosities are MC (0.429), DCE (0.800), TCE (1.20) and the dipole moments<sup>20</sup> are MC (1.14), DCE (1.86), TCE (1.57). The ratios of the polarizabilities are DCE/MC = 0.52 and DCE/TCE = 0.81.

It is noteworthy that the trend with viscosity, in the rate constants for benzyl with TEA in the three solvents (1.6, 2.0, and  $2.8 \times 10^9$  for TCE, DCE, and MC, respectively) is considerably less in magnitude than is expected for the viscosity dependence of diffusion-controlled rate constants. This is consistent with our earlier assertion that these values are lower than  $k_{\text{diff}}$  by a factor of 2 or 3. From the data, it is not possible to identify a single solvent parameter which is responsible for the observed effects. It is clear, however, that the solvent is intimately involved in the reaction, a point which has often been made from comparison with gas-phase ion reaction data. Obviously more work is needed to elucidate any quantitative relationship of rate constant to solvent properties.

The foregoing kinetic effects in the reactions with the amines are summarized in Figure 4 in which they are clearly evident. The large decrease in rate constant at the trisubstituted stage for phenyl substitution is seen. The absence of any significant effect for cyclopropyl substitution at the trisubstituted stage is clear. Trends with the nucleophile are seen, as are solvent effects. The selectivity toward the nucleophile is greatest for trityl cation, which has the lowest rate constants.

Since we have made a comparison of our observed kinetic effect of cyclopropyl substitution with the expectations based

on solvolysis data for cyclopropylcarbenium ions, it is pertinent to comment on the solvolysis data, and to ask whether "stability" of the carbenium ion is, in fact, to be compared with the reactivity we determine directly.<sup>21</sup> The solvolysis reaction



consists of an autoionization step ( $k_3$ ), followed by a fast reaction with the solvent ( $k'_3$ ), such that  $k'_3 \gg k_{-3}[\text{X}^-]$ . The rate-determining step in these solvolysis reactions is the formation of the carbenium ion. Accordingly, the solvolysis rate reflects not an intrinsic property of the carbenium ion (viz, its reactivity), but rather a combination of properties of the compound from which the carbenium ion is formed, of the ion itself, and of the solvent in which the autoionization occurs. The role of the solvent is indeed important, and it is noteworthy that a previous determination<sup>11</sup> of rate constants for the arylcarbenium ions in DCE with halide ions gave diffusion-controlled values, namely,  $6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , whereas solvolysis data would generally lead to the expectation  $k_{\text{benzyl}} > k_{\text{benzhydryl}} > k_{\text{trityl}}$ . Thus, it is not clear that a meaningful relationship exists between the rate of formation of an ion from its precursor and its reactivity toward different nucleophiles.

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