

M.I.T. Quart. Prog. Rept., **50**, 11 (1963); (f) McLean, A. D., *J. Chem. Phys.*, **32**, 1959 (1960).

⁶ Clementi, E., C. Roothaan, and M. Yoshimine, *Phys. Rev.*, **127**, 1618 (1962).

⁷ $K = 1.75$, $\alpha(2s) = -0.559$ au; $\alpha(2p) = -0.312$ au; $\alpha(H) = -0.50$ au.

⁸ For BH $\alpha(2s) = -0.909$ au; $\alpha(2p) = -0.314$ au; $\alpha(H) = -0.591$ au. For BB $\alpha(2s) = -0.920$ au; $\alpha(2p\sigma) = -0.189$ au; $\alpha(2p\pi) = -0.179$ au.

⁹ Newton, M. D., unpublished work. In all diatomics studied (CO, C₂, B₂) $K_{\pi\pi}$ was quite large. In C₂ ³ Σ (internuclear distance that of ethane) $K_{\pi\pi}$ was 6.35, whereas in staggered ethane [Pitzer, R. M., and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 1995 (1963)] the same pair of orbitals (which can now interact with E' and E'' symmetry orbitals formed from the hydrogens) had a relatively normal $K_{\pi\pi}$ of 2.31. It is tempting to speculate that in larger molecules where full valency is used, the $K_{\pi\pi}$ anomaly will disappear.

SECONDARY DEUTERIUM ISOTOPE EFFECTS IN SOLVOLYSES OF SMALL-RING COMPOUNDS*

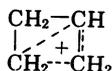
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The importance of nonclassical ions as relatively stable intermediates in S_N1-type reactions is a matter of considerable current controversy.¹ A very important question in this controversy is the extent to which the observed rate accelerations are due to nonclassical electron delocalization in the transition states as compared to high initial state free energies because of steric strain.

The cyclopropylcarbinyl system is one of the numerous examples where high reactivities have been attributed to nonclassical stabilization of the transition state. The cationic reactions of this system have been explained in terms of bicyclobutonium-ion-like intermediates (I).²



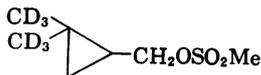
I

Although a considerable amount of experimental data could plausibly be correlated in terms of intermediates like I, the peculiar behavior of this system is still not fully understood. Thus, phenyl substitution on the cyclopropane ring does not cause any very large increase in solvolytic reactivity.³⁻⁵ This marked insensitivity of the rate to phenyl substitution on any other but the α -carbon has also been observed in solvolyses of other compounds where formation of nonclassical ions has been postulated and has been used as an argument against the intermediacy of such ions.^{6, 7}

In continuation of our work on secondary deuterium isotope effects,^{8, 9} compounds II and III have been prepared and their ethanolysis rates measured.



II

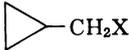
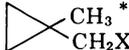
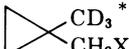
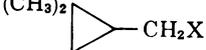
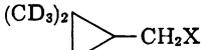


III

If in these reactions an intermediate resembling I is formed, then a considerable amount of positive charge will be displaced to the carbon atoms of the cyclopropane ring in the transition state. Therefore, it might be expected that compounds II and III should behave upon solvolysis analogously to β -deuterium-labeled compounds and would exhibit a rate-retarding kinetic isotope effect.

The results of this investigation are summarized in Table 1 together with some other kinetic data concerning related compounds.

TABLE 1
SOLVOLYSIS RATES OF CYCLOPROPYLCARBINYL METHANESULFONATE AND RELATED METHYL AND METHYL- d_3 SUBSTITUTED COMPOUNDS AT 20° IN 96% ETHANOL

	Compound X = OSO ₂ CH ₃	$k \cdot 10^4 \cdot \text{sec}^{-1}$	Relative rates
V		0.61	1.00
VI		2.88	4.72
II		2.86	4.70
VII		4.53	7.42
VIII		58.2	96
III		59.2	97

* Accompanied by an internal rearrangement to VII, respectively, to the deuterated analogue.

We find that *methyl substitution on the ring produces a considerably larger rate effect than the corresponding phenyl substitution*. However, a methyl group in ring-position 1 produces a smaller rate enhancement (fivefold) than has been previously reported.^{2, 10} A much larger acceleration (100 times) is caused by *gem*-methyl groups in ring-position 2.

We also find that in two critical cases (II and III) the secondary deuterium kinetic isotope effect is negligible.

It is possible that intermediates like I need not be invoked to explain the present data. However, in view of other evidence available on reactions of cyclopropylcarbinyl derivatives, it seems reasonable to explore whether or not our results can be accommodated by nonclassical-ion formation.

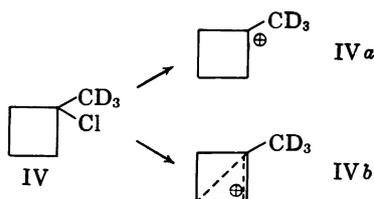
Secondary β -deuterium isotope effects have been ascribed to hyperconjugative electron release from the carbon-hydrogen (-deuterium) bonds in the transition state of the solvolysis reaction.¹¹ The isotope effect is small where this hyperconjugation is hindered or inhibited.^{12, 13}

In terms of nonclassical carbonium ions, the failure to observe a kinetic isotope effect with II and III appears to correspond to the pronounced lack of phenyl substitution on the reaction rates. The usual over-all acceleration caused by a phenyl

group in solvolyses reactions can be regarded as resulting from the combination of two opposing factors, an enhancing resonance effect and a decelerating inductive effect. In general, the former effect is more important than the latter. In order to explain the kinetic data, the possibility must be considered that in the transition state leading to a nonclassical ion resembling I, the usual conjugative stabilization of the incipient positive charge is not very important if the phenyl group is attached to the cyclopropane ring.

Our results can be explained by ascribing the observed rate accelerations to a favorable inductive effect of the methyl groups. The lack of a secondary deuterium isotope effect with II and III can then be interpreted as an absence of hyperconjugative stabilization of the delocalized positive charge by CH_3 - or CD_3 -groups.

To test this interpretation 1-methyl- d_3 -cyclobutyl chloride (IV) was prepared and its solvolysis rate measured.



If in this reaction a classical tertiary carbonium ion (IVa) is formed in the rate-determining step, it can be expected that the kinetic isotope effect will be similar in magnitude to that observed in solvolysis of other β -deuterated halides. If, however, the transition state actually leads to a bicyclobutonium ion (IVb) as suggested by Roberts and co-workers² and if our hypothesis is correct (i.e., that charge delocalization results in a reduced hyperconjugative electron release from the neighboring CH_3 -resp. CD_3 -group), it might be expected that with IV the magnitude of this isotope effect may be significantly reduced.

TABLE 2

KINETIC ISOTOPE EFFECTS IN SOLVOLYSIS OF SOME β -DEUTERIUM-LABELED TERTIARY HALIDE

Compound	Reaction conditions	k_H/k_D
	50% $\text{C}_2\text{H}_5\text{OH}$, 50°	1.09
	80% $\text{C}_2\text{H}_5\text{OH}$, 25°	1.78*
	80% $\text{C}_2\text{H}_5\text{OH}$, 25°	1.41*
	80% $\text{C}_2\text{H}_5\text{OH}$, 25°	2.36*

* Shiner, V. J., Jr., *J. Am. Chem. Soc.*, **75**, 2925 (1953).

The solvolysis rate constants of IV and the undeuterated analogue were measured in 50 per cent ethanol at 50°. The results were $k_H = 8.30 \cdot 10^{-4} \cdot \text{sec}^{-1}$ and $k_D = 7.58 \cdot 10^{-4} \cdot \text{sec}^{-1}$ ($k_H/k_D = 1.09$). In Table 2 the observed isotope effect is compared to those reported for solvolyses of some other tertiary halides. It can be seen that in our case the rate retardation caused by three β -deuteriums (9%) is indeed much smaller than generally observed (40–50%).

Work is in progress to test the scope of the latter observation and the validity of the interpretation.

* Taken in part from the Ph.D. thesis of M. N., University of Zagreb, 1963.

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¹ Brown, H. C., in *The Transition State*, Special Publ. No. 16, Chemical Society, London, 1962, pp. 140–158, 174–178; Brown, H. C., and F. J. Chloupek, *J. Am. Chem. Soc.*, **85**, 2322 (1963); Brown, H. C., and H. M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963); Winstein, S., A. H. Lewin, and K. C. Pande, *J. Am. Chem. Soc.*, **85**, 2324 (1963); Brown, H. C., F. J. Chloupek, and Min-Hon Rei, *J. Am. Chem. Soc.*, **86**, 1247, 1248 (1964). See also refs. 6 and 7.

² Cox, E. F., M. C. Caserio, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2719 (1961), and previous papers.

³ Wilt, J. W., and D. D. Roberts, *J. Org. Chem.*, **27**, 3430 (1962).

⁴ Snee, R. A., K. M. Lewandowsky, I. A. I. Taha, and B. R. Smith, *J. Am. Chem. Soc.*, **83**, 4843 (1961).

⁵ Breslow, R., J. Lockhart, and A. Small, *J. Am. Chem. Soc.*, **84**, 2793 (1962).

⁶ Corey, E. J., and Hisashi Uda, *J. Am. Chem. Soc.*, **85**, 1788 (1963).

⁷ Brown, H. C., F. J. Chloupek, and Min-Hon Rei, *J. Am. Chem. Soc.*, **86**, 1246 (1964).

⁸ Borčić, S., M. Nikoletić, and D. E. Sunko, *J. Am. Chem. Soc.*, **84**, 1615 (1962).

⁹ Nikoletić, M., S. Borčić, and D. E. Sunko, *Abstracts, XIXth International Congress of Pure and Applied Chemistry*, London, 1963, sect. A, p. 26.

¹⁰ In a recent article D. D. Roberts [*J. Org. Chem.*, **29**, 294 (1964)] found only a fourfold rate acceleration in acetolysis of (1-methylcyclopropyl)-carbonyl tosylate relative to cyclopropylcarbonyl tosylate, in agreement with our results.

¹¹ Halevi, E. A., in *Progress in Physical Organic Chemistry* (New York: John Wiley and Sons, 1963), vol. 1, p. 189.

¹² Shiner, V. J., Jr., and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **85**, 2416 (1963).

¹³ Shiner, V. J., Jr., and J. G. Jewett, *J. Am. Chem. Soc.*, **86**, 945 (1964).

SURPLUS FREE POLES OF APPROXIMATING RATIONAL FUNCTIONS*

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Under broad conditions, as expressed in Theorem 1 below, rational functions which approximate on a point set E of the z plane to a function analytic on E and meromorphic in a region containing E have free poles which approach the respective poles of $f(z)$. However, if the rational functions have an excess of free poles, the question arises as to the asymptotic behavior of those poles, and the possible effect on degree of convergence on E and elsewhere if those poles are suppressed.

The present note makes a modest contribution to this study, in both general theory and by specific examples.