

predict the preferred structures of ionophores, artificial molecular receptors, proteins, ..., in solution, even when relative conformations of species with identical binding sites are compared. It also makes it clear that the solvation pattern depends on the very nature of the solvent.¹⁶ Particularly, the bridging position found for some water molecules is likely to be a specificity of that solvent. In mixed solvents containing water, or even when traces of water are present, such bridging water molecules are expected to become part of some of the structures. It is also clear that H_3O^+ , which makes stronger H bonds to ethers than does H_2O , should also influence the conformation of crown ethers^{10,17} and of other flexible

molecules, even in very weakly acid conditions.

Note Added in Proof. For the C_1 conformer, we have rerun a Monte Carlo simulation on a cluster of 250, instead of 100, water molecules. The energy results, after 10^6 moves, are as follows: $E_{\text{ww}} = -6.7$ kcal/mol per water molecule, $E_{\text{sw}} = -53.3$ kcal/mol. They show, as expected, an appreciable improvement of the water-water energy, while the solute-water interaction energy is very close to the previous one, indicating that 100 H_2O already account for the major part of the "solvation" of the 18-crown-6.

Acknowledgment. We thank R. Ripp and J. M. Wurtz for setting up programs on the PS300 computer graphics system at the IBMC, Strasbourg.

Registry No. 18-Crown-6, 17455-13-9.

(16) Mosier-Boss, P. A.; Popov, A. I. *J. Am. Chem. Soc.* **1985**, *107*, 6168.

(17) Sharma, R. B.; Kebarle, P. *J. Am. Chem. Soc.* **1984**, *106*, 3913.

The Infrared Spectrum and Force Field of C_3O

Ronald D. Brown,* David E. Pullin, Edward H. N. Rice, and Martin Rodler

Contribution from the Department of Chemistry, Monash University, Clayton, Victoria, Australia 3168. Received June 4, 1985

Abstract: The infrared spectra of matrix-isolated tricarbon monoxide and six isotopically substituted species have been recorded. C_3O was formed by pyrolyzing fumaroyl dichloride seeded in excess argon. The ν_1 , ν_2 , and ν_4 bands have been observed. A normal coordinate analysis has yielded a general harmonic force field. This has been compared with the force field from ab initio calculations.

We recently reported the pyrolytic generation of tricarbon monoxide and its characterization by its microwave spectrum,¹ followed by further microwave studies of various isotopic variations of the molecule leading to a substitution geometry.² The study was substantially assisted by a preceding theoretical investigation by ab initio molecular orbital methods.³ This provides predictions of force constants and vibrational frequencies, the lowest of which, ν_5 , could be estimated approximately from the l -doubling transitions observed in the microwave spectrum.² It seemed worthwhile to attempt to observe vibrational transitions in the infrared for C_3O by preparing low-temperature argon matrices, particularly since DeKock and Weltner⁴ had tentatively proposed the presence of C_3O among the products obtained by deposition of CO and carbon vapor, mainly C or C_2 , in cold argon matrices. Their evidence was an infrared band at 2244 cm^{-1} , which they assigned as the ν_1 of C_3O .

We now report the successful observation of the IR spectrum of matrix-isolated C_3O , including a number of different isotopic versions yielding a general harmonic force field, and more elaborate ab initio molecular orbital calculations of both vibrational frequencies and intensities that helped in the assignment of the bands.

Experimental Section

Apparatus. A closed cycle cryostat (model 21C cryodyne from CTI cryogenics) was used for all experiments. The cold stage of the cryostat, with which the copper block containing the CsI window was in direct contact, was at 9–10 K. Both deposition of the matrices and measurements of the infrared spectra were carried out at the lowest available temperature. The spectra were recorded in the region $4000\text{--}300\text{ cm}^{-1}$

with a Perkin Elmer 180 spectrophotometer. The instrument was calibrated by measuring reference gases. The absolute frequencies of the absorption maxima are believed to be accurate to within 0.3 cm^{-1} .

Generation of C_3O . Gas mixtures of fumaroyl dichloride and argon (ratio 1:500) were prepared in advance and stored in a 1.6-L bulb at 0.5 atm. The argon used had a stated purity of 99.995%. The matrices were deposited at a rate of 40 mmol of argon per h. The mixtures were pyrolyzed in a silica tube of 16 mm inner diameter. A 30 cm long electric oven was used and the temperature measured with a thermocouple. Under these conditions the optimum temperature for the generation of C_3O was 1100–1200 °C. In some experiments a straight quartz tube was used, the oven ending about 25 cm in front of the cryostat. In order to reduce the influx of radiation from the oven to the CsI window, a 90° bend was later introduced between oven and cryostat. This had no noticeable influence on the yield of C_3O .

Chemicals. The preparation of isotopically enriched fumaroyl dichloride (fumaryl chloride, (*E*)-2-butenediyl dichloride) has been described earlier.² The three enriched samples yielded mixtures of C_3O with the following isotopic ratios: 90% CC^{13}CO + 10% CCCCO , 45% C^{13}CCO + 45% $^{13}\text{CCCCO}$ + 10% CCCCO , and 16% CCC^{18}O + 84% CCCCO .

Molecular Orbital Calculations. To obtain an improved prediction of the infrared spectrum we extended the previously reported ab initio calculations.³ The 6-31G* basis set was used throughout this work. This basis set includes d-polarization functions on all atoms. The off-diagonal force constants were calculated at the Hartree-Fock level (HF) with the MP3/6-31G* geometry reported, while all diagonal force constants were computed at the MP3 level, which includes electron correlation. Due to the regular overshoot of the calculated frequencies a scaling factor of 0.958 was introduced which was obtained from similar calculations on known molecules.⁵ The derivatives of the dipole moment with respect to the geometrical parameters were calculated numerically at the Har-

(1) Brown, R. D.; Eastwood, F. W.; Elmes, P. S.; Godfrey, P. D. *J. Am. Chem. Soc.* **1983**, *105*, 6496–6497.

(2) Brown, R. D.; Godfrey, P. D.; Elmes, P. S.; Rodler, M.; Tack, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4112–4114.

(3) Brown, R. D.; Rice, E. H. N. *J. Am. Chem. Soc.* **1984**, *106*, 6475–6478.

(4) DeKock, R. L.; Weltner, W. *J. Am. Chem. Soc.* **1971**, *93*, 7106–7107.

(5) Brown, R. D.; Rice, E. H. N.; Rodler, M. *Chem. Phys.* **1985**, *99*, 347–356.

Table I. Observed Infrared Transitions (cm^{-1}) of Isotopomers of Tricarbon Monoxide Embedded in an Argon Matrix

isotopomer	assignment	frequency	rel intensity
CCCO	$\nu_1(\Sigma)$	2242.6	s
	$\nu_2(\Sigma)$	1907.2	w
	$\nu_4(\Pi)$	579.6	w
CCC ¹⁸ O	ν_1	2224.2	m
	ν_2	1888.8	vw
	ν_4	575.3	vw
CC ¹³ CO	ν_1	2194.3	s
	ν_2	1898.2	w
	ν_4	563.9	w
C ¹³ CCO	ν_1	2225.7	s
	ν_2	1872.8	w
	ν_4	575.8	w
¹³ CCCO	ν_1	2240.0	s
	ν_2	1886.5	w
	ν_4	579.6	w
C ¹³ C ¹³ CO	ν_1	2174.0	w
¹³ CC ¹³ CO	ν_1	2190.5	w

Table II. Observed and Calculated Relative Intensities of the Fundamentals of C₃O

	obsd	calcd
ν_1	100	100
ν_2	2.3	2.6
ν_3		0.02
ν_4	3.3	3.4
ν_5		0.16

tree-Fock level. This allowed the prediction of the relative intensities of the bands.

Observations

The intensity of the band at 2243 cm^{-1} , which was assigned as ν_1 of C₃O by deKoch and Weltner,⁴ was used to optimize the experimental conditions. (These authors called this highest stretching frequency ν_3 rather than ν_1 .) Figure 1 shows the infrared spectrum of the pyrolysis of unlabeled fumaroyl dichloride under the optimum condition described above. With the use of the ab initio force field the two weak peaks visible besides the strong band at 2243 cm^{-1} could be readily assigned to ¹³C isotopes of C₃O. The definite assignment of other bands to C₃O was not possible without further information. Thus three samples of isotopically enriched fumaroyl dichloride were prepared and their spectra measured after pyrolysis. They allowed the unequivocal assignment of the ν_2 and ν_4 bands which was mainly based on relative intensities and the agreement between observed and calculated frequency shifts. Table I lists all the measured absorption maxima of bands assigned to the different isotopomers of tricarbon monoxide. None of the bands was found to be split due to different crystal fields in different matrix sites, but the intense ν_1 bands show an unresolved tail on the high frequency side. The full width at half maximum of all other bands was 1.0–1.2 cm^{-1} .

Table II contains the measured and calculated relative intensities of the fundamentals of C₃O. The excellent agreement between theory and experiment must be considered fortuitous because the small calculated values result from differences between rather large numbers. The very low intensity calculated for the lowest stretching mode ν_3 explains why it could not be observed. The energy of the lower bending mode was estimated from microwave measurements² to be about 150 cm^{-1} and was thus outside the frequency range used.

General Valence Force Field

The 17 vibrational frequencies listed in Table I were used for the force-field refinement. It was done by fitting the force constants to the observed frequencies of the parent isotopic species and to the frequency shifts between the other isotopomers and the parent species. Due to the different kinds of data the following

Table III. Force Constant Matrix of C₃O Derived from Experimental Data and ab Initio Calculations^a

force constant	exptl ^b	calcd
$F_{1,1}$	16.82 (16)	19.27
$F_{1,2}$	1.85 (16)	1.55
$F_{1,3}$	0.0 ^c	0.00
$F_{2,2}$	10.62 (25)	10.99
$F_{2,3}$	1.05 (12)	0.52
$F_{3,3}$	11.61 (15)	13.12
$F_{4,4}$	0.609 (12)	0.653
$F_{4,5}$	0.014 (8)	0.027
$F_{5,5}$	0.066 ^c	0.066

^aStretching force constants in $\text{mdyn}\cdot\text{\AA}^{-1}$, bending constants in $\text{mdyn}\cdot\text{\AA}$. ^bNumbers in parentheses represent one standard deviation of the fit. ^cNot fitted, transferred from the calculated force field.

weight was attached to each datum: for the frequencies 2% of their value and for the shifts 10% of their value plus 0.2 cm^{-1} . The reported substitution structure² was used for the calculation. The symmetry coordinates were defined as follows:

$$S_1 = r(\text{O}-\text{C}_1)$$

$$S_2 = r(\text{C}_1-\text{C}_2)$$

$$S_3 = r(\text{C}_2-\text{C}_3)$$

$$S_4 = \beta(\text{OC}_1\text{C}_2)$$

$$S_5 = \beta(\text{C}_1\text{C}_2\text{C}_3)$$

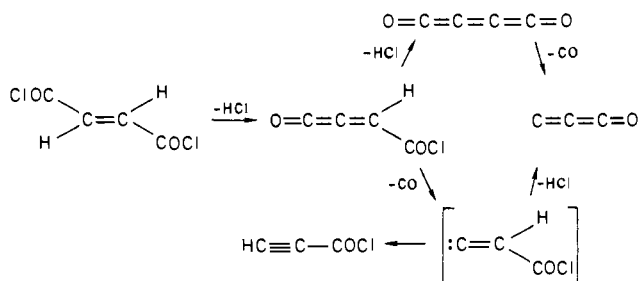
with the atomic numbering scheme C₃C₂C₁O.

The ab initio force constants listed in Table III have been used as starting values for the refinement. Due to the absence of any experimental data for the lowest stretching mode ν_3 , not all 6 force constants of the Σ block could be determined. We therefore decided to fix the interaction constant $F_{1,3}$ because it was least determined by the observed data. It was set to zero as predicted by the molecular orbital calculations.

A similar situation was found in the Π block, where the absence of precise data for the low-lying CCC bending vibration did not allow the determination of $F_{5,5}$. Its value was also transferred from the calculated force field. This seemed justified by the fairly good agreement between the calculated and estimated² frequency of the CCC bending mode. The resulting force constant matrix is shown in Table III; Table IV compares the calculated frequencies and shifts from the experimental and ab initio force field with the observed values.

Discussion and Conclusions

The study of the products of the thermal decomposition of fumaroyl dichloride by matrix isolation infrared spectroscopy has led to the unequivocal observation of the spectrum of tricarbon monoxide. The assignment of the ν_1 band by deKoch and Weltner⁴ in 1971 proves to be correct. Besides C₃O, CO₂, CO, and HCl the pyrolysis yielded many bands which could not easily be assigned to known substances. Of special interest in this context is the potential intermediate C₄O₂. Two possible reaction paths may lead from fumaroyl dichloride to C₃O:

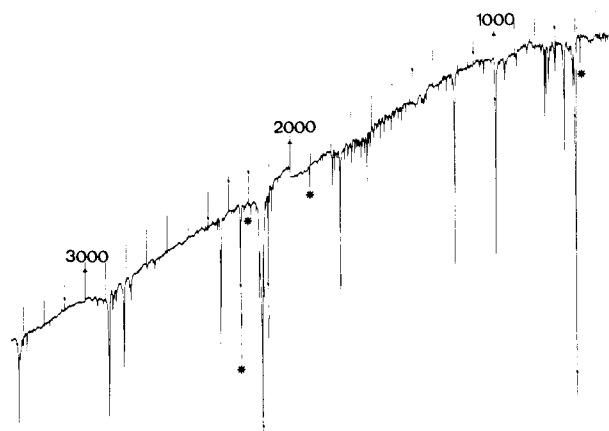


The lack of sufficient amounts of highly enriched isotopes of the dichloride prevented the search for C₄O₂.

The normal coordinate analysis produced a rather complete general harmonic force field. Table V compares some force

Table IV. Observed and Calculated Frequencies or Frequency Shifts for C₃O Isotopes (cm⁻¹)

isotope/mode	obsd	from exptl force	from ab initio force field	from scaled ab initio force field
CCCO				
ν_1	2242.6	2230.7	2411	2310
ν_2	1907.2	1905.6	2036	1950
ν_3		1010	1023	980
ν_4	579.6	579.0	592	567
ν_5		138	138	132
CCC ¹⁸ O				
$\Delta\nu_1$	-18.4	-19.2	-21.1	-20.2
$\Delta\nu_2$	-18.4	-18.4	-20.5	-19.6
$\Delta\nu_4$	-4.3	-4.5	-4.7	-4.5
CC ¹³ CO				
$\Delta\nu_1$	-48.3	-49.2	-51.3	-49.1
$\Delta\nu_2$	-9.0	-9.2	-10.8	-10.3
$\Delta\nu_4$	-15.7	-15.5	-16.0	-15.3
C ¹³ CCO				
$\Delta\nu_1$	-16.9	-17.5	-19.9	-19.1
$\Delta\nu_2$	-34.4	-35.4	-36.6	-35.0
$\Delta\nu_4$	-3.8	-3.9	-3.8	-3.6
¹³ CCCCO				
$\Delta\nu_1$	-2.6	-2.5	-3.6	-3.5
$\Delta\nu_2$	-20.7	-20.5	-21.7	-20.8
$\Delta\nu_4$	0.0	0.0	0.0	0.0
C ¹³ C ¹³ CO				
$\Delta\nu_1$	-68.6	-70.0	-74.6	-71.5
¹³ CC ¹³ CO				
$\Delta\nu_1$	-52.1	-52.9	-56.2	-53.8

**Figure 1.** Infrared spectrum (in cm⁻¹) of matrix-isolated tricarbon monoxide. Bands resulting from tricarbon monoxide are marked with an asterisk.

constants with other oxides of carbon. The CO stretching force constants in CO and C₃O are significantly larger than those in CO₂ and C₃O₂. This might be interpreted by a partial triple bond in the monoxides according to the resonance structures $\text{C}\equiv\text{O}^+$ and $\text{C}\equiv\text{C}-\text{C}\equiv\text{O}^+$. This view is also supported by the shorter CO bond length (CO, 1.128 Å; C₃O, 1.150 Å; CO₂, 1.163 Å, C₃O₂, 1.163 Å). The CCO bending force constants in C₃O₂ and C₃O are very similar while the constant for the CCC bending is an order of magnitude smaller in the former case. But the value for C₃O must be taken with caution due to the lack of precise experimental data for its determination.

Carbon suboxide is known to be a quasi-linear molecule. Rigid bender calculations show⁸ that the bending potential about the central carbon atom is highly anharmonic. In the vibrational

Table V. Comparison of Force Constants of Different Oxides of Carbon^a

diagonal force constant	CO	CO ₂ ^b	C ₃ O ₂ ^c	C ₃ O
CO stretch	18.7	15.3	14.5	16.8
CC stretch			12.4	10.6 ^d
XCO bend		0.76	0.68	0.61
CCC bend			0.0057	0.066

^aStretching constants in mdyn·Å⁻¹ (10⁻² N m⁻¹), bending constants in mdyn·Å (10⁻¹⁸ N m). ^bCalculated from the (IR active) transitions listed in ref 6 plus ν_1 from ref 13. ^cFrom ref 7. ^dCentral C=C bond.

ground state the potential shows a hump of about 31 cm⁻¹ at the linear configuration and the potential minimum corresponds to a structure which is bent by 22° from linearity. Furthermore it has been noted⁹ that the value of the centrifugal distortion constant D_J calculated from the harmonic force field is about 15 times smaller than the observed value (0.078 vs. 1.14 kHz). This was explained by a major contribution from the anharmonic bending vibration. Taking this into account by using the rigid bender model the experimental value could be reproduced very well.⁸ In the case of C₃O the experimentally determined force field listed in Table III yields a distortion constant of 0.465 kHz. The observed value is 0.777 (1) kHz¹⁰ and was derived from the rotational spectrum. Aliev¹¹ showed that an *upper* limit for D_J exists which is independent of the force field but is only determined by the rotational constant and the lowest stretching vibration. Unfortunately this band has not been observed. But if we take the experimental and calculated (scaled) force field the *upper* limit becomes 0.471 and 0.504 kHz, respectively. Both values are well below the experimental one. This might be an indication that the CCC bending potential is rather anharmonic. This view is also supported by the finding that the substitution bond length of the terminal CC bond is considerably smaller than the value predicted by reliable molecular orbital calculations.²

(6) Irvine, M. J.; Mathieson, J. G.; Pullin, A. D. E. *Aust. J. Chem.* **1982**, *35*, 1971-77.

(7) Murthy, A. S. N.; Ranganathan, S. *J. Mol. Struct.* **1982**, *90*, 219-226.

(8) Weber, W. H.; Ford, G. W. *J. Mol. Spectrosc.* **1976**, *63*, 445-458.

(9) Duckett, J. A.; Mills, I. M.; Robiette, A. G. *J. Mol. Spectrosc.* **1976**, *63*, 249-264.

(10) Tang, T. B.; Inokuchi, H.; Saito, S.; Yamada, C.; Hirota, E. *Chem. Phys. Lett.* **1985**, *116*, 83.

A comparison between experimental and calculated data shows that the *ab initio* force constants and intensities are fairly reliable. This justifies their use in cases where constants cannot be determined from experimental data alone. Secondly, it helps in choosing the correct set of force constants between sets which fit the observed data equally well.¹²

(11) Aliev, M. R. *Opt. Spectrosc.* **1971**, *31*, 301-304.

(12) McKean, D. C.; Duncan, J. L. *Spectrochim. Acta* **1971**, *27A*, 1879-1891.

Acknowledgment. This work was supported by the Australian Research Grants Scheme. Dr. M. Rodler acknowledges the assistance of a Monash University Vice-Chancellor's Postdoctoral Fellowship.

Registry No. CCCO, 11127-17-6; CCC¹⁸O, 11127-21-2; CC¹³CO, 11127-20-1; C¹³CCO, 11127-19-8; ¹³CCCO, 11127-18-7; C¹³C¹³CO, 11127-24-5; ¹³CC¹³CO, 11127-23-4; fumaroyl dichloride, 627-63-4.

(13) Herzberg, G. "Infrared and Raman Spectra"; D. Van Nostrand Co.: Princeton, NJ, 1945.

Direct Observation of Ion-Pair Dynamics

J. M. Masnovi and J. K. Kochi*

Contribution from the Chemistry Department, University of Houston, University Park, Houston, Texas 77004. Received July 11, 1985

Abstract: The intimate ion pair [A⁺,T⁻] is spontaneously generated by the charge-transfer excitation of the electron donor-acceptor complex of anthracene donors (A) and tetranitromethane (TNO₂) with a 25-ps laser pulse. The kinetics of the subsequent ion-pair decay to the adduct (i.e., [A⁺,T⁻] → AT) is followed spectroscopically over the separate picosecond, nanosecond, and microsecond time domains, each with a different laser-flash system. Three distinctive rate profiles are observed: (a) the picosecond decay following first-order kinetics (*k_I*), the nanosecond decay also following first-order but slower kinetics (*k_{II}*), and the microsecond decay following second-order kinetics (*k_{III}*). The experimental rate constants *k_I*, *k_{II}*, and *k_{III}* are associated with the relaxation of the intimate or tight ion pair [A⁺,T⁻], the solvent-separated or loose ion pair [A⁺//T⁻], and the free ions [A⁺ + T⁻], respectively, as originally formulated by Winstein and co-workers for solvolysis mechanisms. These kinetics data together with the measurements of the fractional partitioning of ion pairs allow all the microscopic rate constants relevant to ion pair dynamics to be separately evaluated. The Winstein ion-pair formulation is substantiated by the observation and quantitative treatment of the "common-ion" and "special" salt effects. The role of solvent is underscored by the unique kinetics responses of reactive and persistent cations derived from various 9-substituted and 9,10-disubstituted anthracenes, respectively, with changes in the polarity of the medium from benzene and dichloromethane to acetonitrile. The overall importance of charge annihilation and separation in the microdynamics of transient ion pairs is underscored by a comparison with the bimolecular kinetics of radical-radical interaction measured under comparable conditions.

Ions and ion pairs are fundamental to our understanding of a wide variety of organic reaction mechanisms in solution.¹ Much of the knowledge about the behavior of stable ions derives largely from static conductometric measurements.² More recently, magnetic techniques such as NMR and ESR spectroscopy have been used to describe ion pairing and aggregation effects—principally still within a thermodynamic context.³ Our understanding of the *dynamic* behavior of reactive ions and ion pairs stems largely from the pioneering investigations of solvolytic reactions by Winstein and co-workers.⁴⁻⁷ Their elegant analysis

of the solvolysis kinetics and observation of the "special" salt effects have led to the seminal concept of intimate and solvent-separated ion pairs as key reactive intermediates. Owing to the complexity of the kinetics, however, the general solutions of the rate expressions have not been sufficient to yield the microscopic rate constants for the various ion-pair dynamics.⁸

The development of laser-flash photolytic techniques especially on the picosecond time scale, now provides the experimental means to directly observe the complete spectrum of ion-pair dynamics.^{9,10} Crucial to these studies is the spontaneous production of an ion pair in sufficient concentrations and in a discrete electronic state as well as geometric configuration to measure the relaxation kinetics in a homogeneous system.¹¹ We believe that the pro-

(1) (a) Hammett, L. P. "Physical Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1970. (b) Kosower, E. M. "An Introduction to Physical Organic Chemistry"; Wiley: New York, 1968. (c) Lowry, T. H.; Richardson, K. H. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper & Row: New York, 1981. (d) Szwarc, M., Ed. "Ions and Ion Pairs in Organic Reactions"; Wiley-Interscience: New York, Vol. 1, 1972; Vol. 2, 1974.

(2) See, e.g.: (a) Schiavo, S.; Fuoss, R. M.; Marrosu, G.; Guida, G. *J. Solution Chem.* **1979**, *8*, 557 and references therein. (b) D'Aprano, A. *J. Solution Chem.* **1974**, *3*, 363. (c) Kaneko, H.; Wada, N. *J. Solution Chem.* **1978**, *7*, 19.

(3) For a review, see ref 1d, Chapters 5-8 in Vol. 1, p 177 ff.

(4) (a) Winstein, S.; Klinedinst, P. E., Jr.; Robinson, G. C. *J. Am. Chem. Soc.* **1961**, *83*, 885. (b) Winstein, S.; Klinedinst, P. E., Jr.; Clippinger, E. J. *Am. Chem. Soc.* **1961**, *83*, 4986. (c) Winstein, S.; Robinson, G. C. *J. Am. Chem. Soc.* **1958**, *80*, 169 and related papers. For reviews see: (d) Harris, J. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 89. (e) Reference 1d, Vol. 2, Chapter 3, p 247 ff.

(5) Weiner, H.; Sneen, R. A. *J. Am. Chem. Soc.* **1965**, *87*, 287, 292. Sneen, R. A.; Larsen, J. W. *J. Am. Chem. Soc.* **1966**, *88*, 2593. Ogg, R. A., Jr.; Polanyi, M. *Trans. Faraday Soc.* **1935**, *31*, 604.

(6) (a) Goering, H. L.; Briody, E. G.; Levy, J. F. *J. Am. Chem. Soc.* **1963**, *85*, 3059. Goering, H. L.; Levy, J. F. *J. Am. Chem. Soc.* **1964**, *86*, 120. Young, W. G.; Winstein, S.; Goering, H. L. *J. Am. Chem. Soc.* **1951**, *73*, 1958. (b) Crampton, M. R.; Grunwald, E. *J. Am. Chem. Soc.* **1971**, *93*, 2987.

(7) See: Shiner, V. J., Jr.; in "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. W., Eds.; Van Nostrand Reinhold: New York, 1970.

(8) Rather than individual rate constants, their ratios predominate.

(9) For example, see: Barbara, P. F.; Brus, L. F.; Rentzepis, P. M. *Chem. Phys. Lett.* **1980**, *64*, 447. Hochstrasser, R. P. *Pure Appl. Chem.* **1982**, *52*, 2683. Wang, Y.; Crawford, M. C.; Eisenthal, K. B. *J. Phys. Chem.* **1980**, *84*, 2696.

(10) (a) Simon, K. D.; Peters, K. S. *Acc. Chem. Res.* **1984**, *17*, 277. (b) See also: Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 1441.

(11) For example, flash photolysis of solvolytic systems have not been found to be useful since they are usually beset with a number of problems, including extraneous excited states and/or long-lived byproducts.¹²