

Figure 2. Electric field effect on the "polarized" (P) and "unpolarized" (U) portions of a KD_2PO_4 sample near T_c .

± 0.5 K below T_c , only the P signals persist, with no further significant change down to 77 K. Earlier studies^{3-6,13} in the ferroelectric phase have shown that these two P-type signals represent the two possible (positively and negatively charged) domains of electric polarization below T_c . Figure 1b shows the temperature variation of the intensity of the P and the U signals. The rather rapid variation observed suggests that it is related to the cooperative ordering near T_c .

That the P signals are detected about 3 K above T_c , that their intensity increases rapidly as $T \rightarrow T_c$, and that these are the only signals well below T_c imply the following picture as the lattice approaches T_c : As $T \rightarrow T_c$ (from $T > T_c$), the paraelectric phase lattice starts to grow small "islands" in which the local symmetry corresponds to that of the ferroelectric phase. These "ferroelectric phase islands" then grow in size as $T \approx T_c$, and finally at $T < T_c - 3$, these "islands" cover the complete lattice, which is then fully polarized. It must be mentioned that such predictions have been made recently via molecular dynamic computer simulations.¹⁰ Evidence for such behavior was shown in an earlier NQR study on KH_2AsO_4 ,^{11,12} but of course, the corresponding studies cannot be carried out on the phosphates because of the zero quadrupole moment of ^{31}P .

To verify that the P signals are related to "long-range" ordering regions and not simply to the freezing of some molecular motion on the EPR time scale, we studied the effect of an externally applied electric field.¹³ The basis of this experiment was that while an electric field of only small ($\sim 2-3$ kV/cm) intensity could "polarize" the crystal by reorienting all molecules into a single ferroelectric domain,¹³ orders of magnitude higher electric fields would be needed to reorient an isolated molecule.^{1,13} Since the polar axis of KD_2PO_4 is along c , electric fields of intensity E up to ± 5 kV/cm were applied along this direction.¹¹ As shown in Figure 2, $E \sim 2$ kV/cm was sufficient to polarize the unpolarized part of the sample, since the U signal also changes into the remaining P signal. By reducing E it was possible to control the ratio of the polarized to the unpolarized portions and hence influence and observe the rate of growth of these long-range clusters. Similar electric field effects have been previously reported for the ^{75}As NMR spectrum in KH_2AsO_4 .^{11,12}

The electric field effect not only provides a strong support for the molecular dynamics (i.e., cluster) model of structural phase transitions but also provides a measure of the energy difference between the molecules in the paraelectric and ferroelectric phases near T_c (~ 2 kV/cm was the field necessary to polarize the whole crystal). Moreover, from the widths and separation of the two

P components at $T \ll T_c$ we estimate that a molecule in a typical cluster has a lifetime of $\geq 10^{-8}$ s at 2 K above T_c . Furthermore, the detection of the coexistence of the two phases around T_c suggests that the transition in KD_2PO_4 is of the first order. The generally made statement¹ for the KD_2PO_4 transition is that it is second order but close to being first order (see, however, ref 14).

Another important conclusion is that for studying the lattice fluctuations near T_c of the KH_2PO_4 -type compounds via EPR, the electronic charge and site symmetry of the paramagnetic probe must match those of the substituted group in the host, since earlier studies^{5,7} of KD_2PO_4 using AsO_4^{4-} and CrO_4^{3-} probes (which, as mentioned here earlier, do not match the PO_4^{3-} units) did not detect changes near T_c such as detected here with SeO_4^{3-} . This conclusion can be verified by similar studies on KD_2AsO_4 and the many other members of this family.¹ Another critical experiment would be to study the antiferroelectrics $\text{ND}_4\text{D}_2\text{PO}_4$, $\text{ND}_4\text{D}_2\text{AsO}_4$, and their undeuterated analogues. We predict that such clusters would be observed via CrO_4^{3-} , but not by using SeO_4^{3-} or AsO_4^{4-} , since ENDOR studies^{5,8} have shown that, of these three, only CrO_4^{3-} meets the charge and symmetry requirements for antiferroelectric lattices. We believe that the results reported here bear on some important and novel features of critical fluctuations and should stimulate further experimental and theoretical work on the microscopic picture of cooperative phenomena.

Acknowledgment. This research was supported in part by grants from the Research Corp., National Science Foundation, and the Energy Research Center of West Virginia University.

Registry No. KD_2PO_4 , 13761-79-0; SeO_4^{3-} , 35473-43-9.

(14) It was pointed out by a referee that because of the very different masses of P and Se the EPR spectra may not reflect the true long-range order of the undoped lattice. This is true for impurities in general, so all impurity results must be cautiously interpreted. In the present case the temperature dependence of the EPR intensity of the P signals parallels that of high (microwave) frequency dielectric constant. Since the SeO_4^{3-} concentration is low ($\leq 1\%$), the dielectric constant should reflect the behavior of the bulk of the crystal. On this basis it is felt that the SeO_4^{3-} probe senses the lattice ordering perhaps fairly faithfully. We thank the referee for highlighting this point, which we plan to discuss in detail in a forthcoming publication.

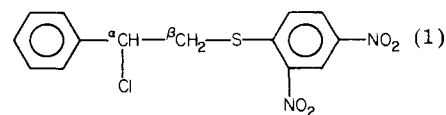
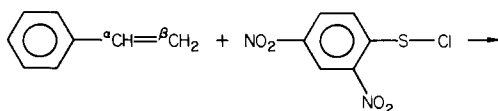
Carbon-14 Isotope Effects in the Addition of 2,4-Dinitrobenzenesulfonyl Chloride to Styrene-1- ^{14}C and Styrene-2- ^{14}C

Marianna Kanska and Arthur Fry*

Department of Chemistry, University of Arkansas
Fayetteville, Arkansas 72701

Received May 12, 1982

As the first reported example of a carbon isotope effect in a simple electrophilic addition reaction, we have found that there are substantial kinetic isotope effects in the addition of 2,4-dinitrobenzenesulfonyl chloride to both α (styrene-1- ^{14}C) and β (styrene-2- ^{14}C) carbon-14 labeled styrenes (eq 1-3).



$$^{12}\text{k}/^{14}\text{k} \text{ for } ^{\alpha}\text{C} = 1.022 \pm 0.0034 \quad (2)$$

(10) See, for example: Schneider, T.; Stoll, E. *Phys. Rev. Lett.* **1978**, *41*, 964. Ogita, N.; Veda, A.; Matsubara, T.; Matsuda, H.; Yonezawa, F. *J. Phys. Soc. Jpn., Suppl.* **1969**, *26*, 145.

(11) Blinc, R.; Bjorkstam, J. L. *Phys. Rev. Lett.* **1969**, *23*, 788.

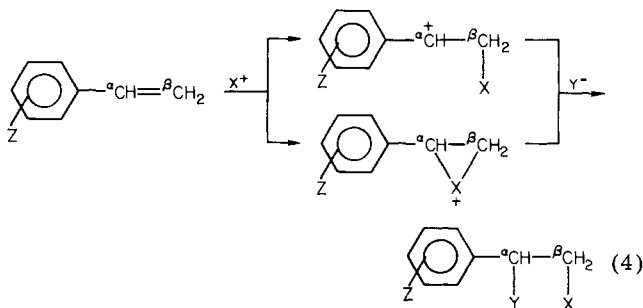
(12) Bjorkstam, J. L. *Adv. Mag. Reson.* **1974**, *7*, 1.

(13) For an experimental procedure for applying electric field and its manifestation in the EPR spectra of paramagnetic probes in ferroelectric crystals, see: (a) Dalal, N. S.; McDowell, C. A.; Srinivasan, R. *Phys. Rev. Lett.* **1970**, *25*, 823. (b) Truesdale, R. D.; Poole, C. P., Jr.; Farrach, F. A. *Phys. Rev.: Condens. Matter* **1982**, *25*, 474 and references therein.

$$^{12}k/^{14}k \text{ for } ^\beta\text{C} = 1.032 \pm 0.0032 \quad (3)$$

We have been puzzled for many years¹ about the reported² lack of a carbon kinetic isotope effect in the addition of bromine to ^{13}C and ^{14}C carbon-14 labeled styrene and methyl cinnamate. All of the mechanisms proposed for these electrophilic addition reactions involve substantial bonding changes at $^\beta\text{C}$ and (perhaps—see below) at $^\alpha\text{C}$ in the rate-determining steps, and these changes should be reflected in carbon isotope effects. Since the main action involved is bond formation, it might be anticipated that the isotope effects would be small. We have suggested¹ that the reported² lack of an isotope effect might be due to a balancing (accidental canceling) of bond formation and bond rupture effects and that the balance point might be changed by using substituted styrenes. The lack of a carbon isotope effect in these simple electrophilic addition reactions is particularly puzzling because other types of addition reactions to alkenes³ (cycloadditions, catalytic hydrogenation, ozonization) give carbon isotope effects as expected.

Much is known about the mechanisms of alkene electrophilic addition reactions,^{4,5} and there is considerable⁵⁻¹⁴ (but disputed¹⁵) evidence that styrene bromination (in contrast to that of simple aliphatic alkenes) has an open carbenium ion-like activated complex, whereas additions of arenanesulfonyl chlorides^{5,12,15-17} to styrenes have cyclic activated complexes (eq 4). Clearly the π



bond breaks and a new bond is formed to $^\beta\text{C}$ in both cases, so a $^\beta\text{C}$ isotope effect should be observed for both mechanisms. At

$^\alpha\text{C}$ exactly the same comment applies for the cyclic mechanism, but for the open carbenium ion mechanism, the $^\alpha\text{C}$ hybridization remains sp^2 and the bonding decrease due to rupture of the double bond will certainly be compensated for, to some extent at least, by increased delocalization of the charge into the ring. Certainly for the open carbenium ion mechanism the $^\alpha\text{C}$ isotope effect should be lower than the $^\beta\text{C}$ effect and could perhaps be nil.

The open carbenium ion mechanism for the bromination of styrenes is supported by the large negative Hammett plot ρ value,^{8,13} about -4.5 with use of σ^+ , the nonstereospecific bromination of β -methylstyrenes,¹⁴ and the very small inverse secondary α -deuterium isotope effects¹⁰ (as would be expected for the no hybridization change argument above). However, there appears to be some concave upward curvature of the Hammett plot for styrenes containing strong electron-withdrawing groups,⁷ and *p*-nitrostyrene shows a significantly lower (more inverse) secondary α -deuterium isotope effect.¹⁰ These facts are interpreted by the authors to mean that for these compounds there is an incursion of a bromonium ion component into the reaction path. (And we think this will probably be reflected in an increased $^\alpha\text{C}$ isotope effect.)

The cyclic nature of the activated complex for additions of arenanesulfonyl halides to styrenes is supported by rate-structure correlations (Hammett $\rho = -2.4$ for addition of 2,4-dinitrobenzenesulfonyl chloride to substituted styrenes^{18,19}) nearly exclusive anti stereospecific additions,²⁰ and direct observations of thiranium ions.^{4,5} On the basis of a reasonably good correlation between the rates of addition of bromine and arenanesulfonyl chlorides, Schmid and Tidwell conclude¹⁵ that cyclic intermediates are involved in both reactions. (It should be noted that substituted styrenes were not used in this correlation and that the fit of the styrene point to the correlation line leaves something to be desired. In view of the substantially different Hammett ρ values for the two reactions, it seems unlikely that the correlation for all the styrenes will be very good.)

The isotope effect results reported above represent our first step in a general study of the mechanisms of simple electrophilic addition reactions by isotope effect techniques using the successive labeling approach.²¹ The addition of 2,4-dinitrobenzenesulfonyl chloride to styrene was chosen as a "calibration case" for the cyclic mechanism. The observed isotope effects at $^\alpha\text{C}$ and $^\beta\text{C}$ are fully consistent with the cyclic mechanism and probably inconsistent with the open carbenium ion mechanisms, in accord with the factors discussed above. Future research will involve expansion of these studies to substituted styrenes and other electrophilic addition reactions, particularly bromination. If the mechanism switches over to the open carbenium ion type, decreased $^\alpha\text{C}$ isotope effects are to be expected. We also plan to carry out calculations of the isotope effects to be expected under various mechanistic assumptions.

The carbon-14 labeled styrenes were prepared by the sodium ethoxide promoted elimination of trimethylamine from the α - and β -labeled (2-phenylethyl)trimethylammonium bromides. The quaternary salts were prepared from the amines, which, in turn, were prepared by lithium aluminum hydride reduction of the labeled phenylacetone nitriles. The nitriles were obtained by reaction of cyanide ion (carbon-14 labeled for β -labeled styrene) with benzyl chloride. The benzyl- ^{14}C chloride needed for preparation of the α -labeled styrene was obtained by lithium aluminum hydride reduction of commercial benzoic- ^{14}C acid followed by treatment of the benzyl alcohol with hydrogen chloride and zinc chloride.

The addition reactions of 2,4-dinitrobenzenesulfonyl chloride to α - and β -carbon-14 labeled styrenes were carried out in anhydrous acetic acid¹⁸ at 30.1°C under a blanket of dry nitrogen. The desired fractions of reaction were obtained by using appropriate limited amounts of 2,4-dinitrobenzenesulfonyl chloride. The

(1) Fry, A. In "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand Reinhold: New York, 1970; pp 364-414.

(2) Ropp, G. A.; Raaen, V. F.; Weinberger, A. J. *J. Am. Chem. Soc.* **1953**, *75*, 3694-3697.

(3) Collins, C. J.; Benjamin, B. M.; Kabalka, G. W. *J. Am. Chem. Soc.* **1978**, *100*, 2570-2571. Benjamin, B. M.; Collins, C. J. *Ibid.* **1973**, *95*, 6145-6146. Bonner, W. A.; Collins, C. J. *Ibid.* **1953**, *75*, 3693-3694, 4516-4518.

(4) de la Mare, P. B. D. "Electrophilic Halogenation"; Cambridge University Press: Cambridge, 1976. Lowry, T. H.; Richardson, K. S. "Mechanism and Theory in Organic Chemistry", 2nd ed.; Harper and Row: New York, 1981; pp 506-530.

(5) For a recent review see: Schmidt, G. H.; Garrett, D. G. In "The Chemistry of Double-Bonded Functional Groups"; Supplement A; Patai, S., Ed.; Wiley: New York, 1977; Chapter 9.

(6) Ruasse, M. F.; Dubois, J. E.; Argile, A. *J. Org. Chem.* **1979**, *44*, 1173-1175.

(7) See Ruasse et al. (Ruasse, M. F.; Argile, A.; Dubois, J. F. *J. Am. Chem. Soc.* **1978**, *100*, 7645-7652) for a good review and leading references.

(8) Pincock, J. A.; Yates, K. *Can. J. Chem.* **1970**, *48*, 2944-2947. Yates, K.; McDonald, R. S.; Shapiro, S. A. *J. Org. Chem.* **1973**, *38*, 2460-2464.

(9) Schmid, G. J. *J. Org. Chem.* **1978**, *43*, 777-778.

(10) Wilkins, C. L.; Regulski, T. W. *J. Am. Chem. Soc.* **1972**, *94*, 6016-6020. Other deuterium isotope effect studies of addition reactions are summarized in this paper.

(11) Charton, M.; Charton, B. I. *J. Org. Chem.* **1973**, *38*, 1631-1636.

(12) Modro, A.; Schmid, G. H.; Yates, K. *J. Org. Chem.* **1977**, *42*, 3673-3676.

(13) Dubois, J. E.; Schwarcs, A. *Tetrahedron Lett.* **1964**, 2167-2173.

(14) Fahey, R. C.; Schneider, H. J. *J. Am. Chem. Soc.* **1968**, *90*, 4429-4434.

(15) Schmid, G. H.; Tidwell, T. T. *J. Org. Chem.* **1978**, *43*, 460-463.

(16) Toyoshima, T.; Okuyama, T.; Fueno, T. *J. Org. Chem.*, **1978**, *43*, 2789-2792.

(17) For an opposing view, see: Kartashev, V. R.; Bodrikov, I. V.; Skorobogatova, E. V.; Zefirov, N. S. *Phosphorus Sulfur Chem.* **1977**, *3*, 213-220.

(18) Orr, W. J.; Kharasch, N. *J. Am. Chem. Soc.* **1956**, *78*, 1201-1206.

(19) We have preliminary data, although at a different temperature, that supports this value from the work of Orr and Kharasch.

(20) Schmid, G. H.; Csizmadia, V. M. *Can. J. Chem.* **1966**, *44*, 1338-1341.

(21) Fry, A. *Pure Appl. Chem.* **1964**, *8*, 409-419.

starting styrene and that recovered after partial reaction were converted quantitatively to styrene dibromide for radioactivity determination. The radioactivity of the addition product was measured directly. All radioactivity measurements were made by liquid scintillation counting with a Beckman DPM-100 instrument and a dioxane based cocktail solution by use of the external standard ratio method. The values of $^{12}k/^{14}k$ reported above are averages (and standard deviations) of values for five different fractions of reaction ranging from 20% to 70% with the calculations being made by all four of the Tong and Yankwich equations^{22,23} for each fraction of reaction. There were no trends in the $^{12}k/^{14}k$ values as the fraction of reaction varied, and as can be seen by the low standard deviations, there was good agreement among the values calculated by the four equations. We take these two facts to indicate that the starting materials were of high chemical and radiochemical purity and that the procedures used in the isotope effect experiments were accurate and properly controlled.

Acknowledgment. We are indebted to Dr. John R. I. Eubanks for preparation of the benzyl-7- ^{14}C chloride and to Professor L. B. Sims for many helpful discussions. Support of this research by National Science Foundation Grant CHE-80-1-16398 is gratefully acknowledged.

Registry No. 2,4-Dinitrobenzenesulfonyl chloride, 528-76-7; styrene, 100-42-5; ^{14}C , 14762-75-5.

(22) Tong, J. Y.; Yankwich, P. E. *J. Phys. Chem.* **1957**, *61*, 540-543.

(23) In two cases for the α -labeled styrene, the styrene recovered after partial reaction polymerized, so its activity could not be determined; in these two cases, only one of the four equations could be used.

Electrooxidative Catalysis Using Dispersed Alumina on Glassy Carbon Surfaces¹

Jerzy Zak and Theodore Kuwana*

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received June 17, 1982

We have long stressed the importance of cleaning and polishing carbon electrode surfaces with small particle abrasives such as alumina and of completely removing these particles from the surface via ultrasonic cleaning.² We have felt that the presence of such particles on surfaces led to irreproducibility and had deleterious effects on the rate of electron transfer. Recently, much to our surprise, we have found that the presence of alumina particles dispersed on glassy carbon surfaces would strongly adsorb compounds such as catechols and catalyze their oxidation. The observed catalysis makes possible the electrochemical differentiation and analysis^{3,4} of the various catechols in the presence of ascorbic acid. Previously, this has been very difficult.

In a typical experiment for the catalysis of catechol, a glassy carbon electrode (Bioanalytical Systems glassy carbon mounted in Kel-F sheath or a Tokai glassy carbon GC-10 in disc form) is prepolished by using alumina (Buehler α -alumina, 1.0, 0.3, and 0.05 μm). After cleaning in an ultrasonic bath with distilled water, the electrode is lightly repolished by using 1.0- μm α -alumina and rinsed with water. The electrode is immediately immersed into the catechol-containing solution. The current-potential (i - E) waves resulting from successive cyclic voltammetric (CV) scans at varying scan rates using this electrode in a solution containing

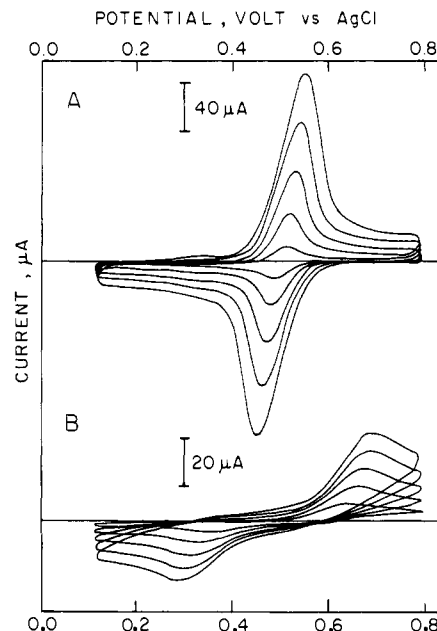


Figure 1. Cyclic voltammograms of alumina dispersed (A) and "clean" glassy carbon (B) electrodes for 5×10^{-4} M catechol in 0.1 M phosphate buffer at pH 2.0: scan rates 0.400, 0.256, 0.144, 0.064, and 0.016 V/s; geometric surface area of carbon, 0.071 cm^2 .

5×10^{-4} M of catechol in 0.1 M phosphate buffer at pH 2.0 are shown in Figure 1A. The shape of the i - E waves is characteristic of the electrolysis of a strongly adsorbed electroactive species.⁵ In addition to the shape, the peak potential is dramatically shifted in comparison to those obtained at a "clean" electrode (see Figure 1B). These uncatalyzed, irreversible waves were taken with a "clean" glassy carbon electrode that had been cleaned ultrasonically and not repolished with alumina. The peak potentials for the catalyzed oxidation (anodic peak potential, E_{pa}) and reduction (cathodic peak potential, E_{pc}) are shifted ca. 150 mV from the uncatalyzed ones obtained on "clean" carbon. The i - E waves for the adsorbed catechols persisted when the electrode was transferred to an electrolyte solution that did not contain any catechol.

Examinations of the clean and the alumina-repolished carbon by scanning electron microscopy (SEM) clearly show the absence and the presence of dispersed alumina particles on the carbon surface. The α -alumina particles are ca. 1 μm in diameter and are dispersed as single and clustered particles. The estimated surface covered by alumina for a typical repolished electrode was ca. 30%. X-ray photoelectron and scanning Auger spectroscopy also confirmed the presence of alumina on the surface.

To study the extent of catechol adsorption caused by the presence of alumina, we recorded CV scans for various concentrations of catechol. At low concentrations such as 5×10^{-5} M, the anodic and cathodic i - E waves were symmetric, and for a freshly immersed electrode, the peak currents would continue to grow with successive cycles until a maximum value was attained. The peak separation between E_{pa} and E_{pc} was 10-12 mV at a scan rate of 100 mV/s and the full width at half-height of either wave was ca. 60 mV. The maximum i - E wave was assumed to correspond to that for a saturation coverage of catechol on the alumina surface. The peak current for this maximum, $i_{p,max}$, varied linearly with scan rate as expected for an electrode reaction of a strongly adsorbed redox species.⁵ If the concentration of catechol in the solution increased while the scan rate was kept constant, the shape of the i - E wave became more characteristic of a reversible, diffusion-controlled redox reaction. Thus, at intermediate values of concentration such as 0.5 to 1.0 $\times 10^{-3}$ M, the i - E wave is a result of the convolution of the two currents due to the adsorbed and the diffusing catechol.

(1) The financial support of this work by the National Science Foundation is gratefully acknowledged.

(2) Evans, J. F.; Kuwana, T. *Anal. Chem.* **1979**, *51*, 348.

(3) (a) Adams, R. N.; *Anal. Chem.* **1976**, *48*, 1126A-1127A. (b) Cheng, Y. Y.; Strope, E.; Adams, R. N. *Ibid.* **1979**, *51*, 2243. (c) Kissinger, P. T.; Hart, J. B.; Adams, R. N. *Brain Res.* **1973**, *55*, 209-213.

(4) (a) Lane, R. F.; Hubbard, A. T. *Anal. Chem.* **1976**, *48*, 1287. (b) Dayton, M. A.; Ewing, A. G.; Wightman, R. M. *Ibid.* **1980**, *52*, 2392.

(5) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods, Fundamentals and Applications"; Wiley: New York, 1980; pp 523-525.