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Observation of the Time Evolution of Phase Changes in Clusters

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We herewith report observations of transformations of molecular clusters from one form to another. Both freezing and solid-state transitions have been monitored. The clusters investigated were produced in a medium of carrier gas in supersonic flow through a miniature Laval nozzle. Structures of the 10-nm clusters generated were probed by electron diffraction at various intervals downstream with a time-of-flight resolution of approximately a microsecond.

Of the more than four dozen substances so far examined in conventional studies,[1-3] one-fifth have yielded molecular clusters exhibiting two or more structural forms (phases). Computer analyses of the nonequilibrium gas dynamics for such cases gave clues that the final form seen might not be the form initially nucleated.[3] Therefore it seemed worthwhile to examine the time dependence of the diffraction patterns of clusters leaving the nozzle.

One experimental feature that simplifies observations is the recently installed pulsed nozzle source.[4] This source makes it possible to eliminate the skimmer which previously separated the nozzle chamber from the diffraction chamber. Dispensing with the skimmer not only avoids degradation of the supersonic jet but also makes it possible to observe the cluster beam 50 μs closer to the source. How soon the clusters can be examined after nucleation depends, of course, upon the nozzle geometry. In the present experiments, the time is about 40 μs with Ne carrier gas but could be much shorter.

Preliminary results for the freezing of CCl_4 are shown in Figure 1. Other transformations observed include the freezing of 1,1,1-trichloroethane and 2,2-dichloropropane and solid-state transitions of *tert*-butyl chloride and selenium hexafluoride.

It can be shown that clusters are comparatively warm during condensation but subsequently experience a precipitous temperature drop in the adiabatically expanding carrier gas.[2] Cooling may be of the order of 100 °C in a few dozen microseconds. Fortunately, the temperature levels off markedly during the stage of flow under observation. This is shown by the appreciable lag of cluster velocities behind those of the molecules of carrier gas.[5] When the expansion becomes rarified, the cessation of momentum exchange with the carrier can be envisaged as if it occurred at a hypothetical "quitting surface".[6] The position of this surface can be inferred from the velocity lag.[7] Under representative conditions in the present work, it is appreciably inside the nozzle exit. By the time the clusters leave the nozzle, they have already attained their evaporative cooling temperature[8,9] or have fallen below it if the subject mole fraction is low and the initial carrier pressure, high. Any further cooling, therefore, is comparatively slow. The warming of individual clusters undergoing a phase change does not influence other clusters.

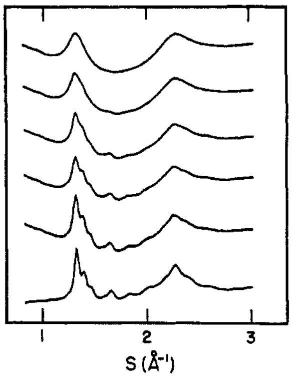

Figure 1. Time evolution of electron diffraction patterns of clusters of carbon tetrachloride nucleated in a supersonic jet with neon carrier. The upper five traces show the freezing of liquid clusters, supercooled by approximately 75 °C, at 5-μs intervals beginning 20 μs after clusters have left the nozzle (top curve). Initial pressure, 1.4 bar; subject mole fraction, 0.125; nozzle throat diameter, 0.0115 cm. Lowest trace: pattern of a sample more completely frozen by a 3.4-fold increase in concentration of carrier gas.

In the case of crystals whose lattice constants are known functions of temperature, it is possible to determine cluster temperatures directly from the diffraction patterns. Sizes can be estimated from the breadths of the diffraction rings.

The present study is not the first electron diffraction investigation of the kinetics of phase change, nor are the microsecond times fast compared with those seen in the earlier (picosecond) observations of the melting of thin metal films by intense laser pulses.[10] Neither is this study the first to observe phase transitions in clusters at various positions in a supersonic jet. An elegant study of high-pressure nitrogen jets by stimulated Raman loss spectroscopy reported equilibrium freezing and solid-state transitions in clusters of N_2 as they cooled.[11] The present research does, however, offer the opportunity of observing spontaneous changes in greatly supercooled clusters, not changes induced by sudden and extreme external perturbations or by rapid equilibrium rearrangements. What is measured corresponds to the rate of appearance of critical nuclei for transitions in substantially supercooled clusters, not the rate of propagation of transitions across clusters.

Several potentially interesting problems can be addressed by the present technique. One hypothesis that has proven useful in the past is the "step rule" or "law of successive reactions" formulated by Ostwald a century ago.[12] It maintains that when a system passes from a less stable form, it does not pass directly into the most stable of the possible phases but, rather, into the next more stable and so, step by step, into the most stable. Apparent exceptions have been rationalized by supposing that the speed of some transformations makes intermediate phases unobservable. The current approach affords an enormously faster and more delicate technique for detecting intermediate transformations than has heretofore been available.

Another application might be to apply the kinetic theory of phase changes of very small particles[13-16] to observed rates of transition. From such an approach could be derived experimental values for the interfacial free energy per unit area between two condensed phases, one or both of which are solid. This subtle parameter of nucleation theory is extremely difficult to measure and far from trivial even to define theoretically. Yet it appears in another theory describing the effect of particle size on the temperature of phase transitions.[17,18] Refinements of the present

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(1) Bartell, L. S. *Chem. Rev.* **1986,** *86,* 492-505.

(2) Bartell, L. S.; Harsanyi, L.; Valente, E. J. *NATO ASI Ser., Ser. B* **1988,** *158,* 37-42.

(3) Bartell, L. S.; Harsanyi, L.; Valente, E. J. *J. Phys. Chem.* **1989,** *93,* 6201-6205.

(4) Bartell, L. S.; French, R. J. *Rev. Sci. Instrum.* **1989,** *60,* 1223-1227.

(5) Schwartz, M. H.; Andres, R. P. *J. Aerosol. Sci.* **1976,** *7,* 281-296.

(6) Sikora, G. S. Ph.D. Thesis, Princeton University, 1973.

(7) Time-of-flight measurements of the velocity lags in this laboratory agree well enough with the lags predicted by the theory of ref 5 to give confidence in the interpretation.

(8) Gspann, J. In *Physics of Electronic and Atomic Collisions;* Datz, S., Ed.; Hemisphere: Washington, 1976.

(9) Klots, C. *J. Phys. Chem.* **1988,** *92,* 5864-5868.

(10) Williamson, S.; Mourou, G.; Li, J. M. C. *Phys. Rev. Lett.* **1984,** *52,* 2364-2367.

(11) Beck, R.; Nibler, J. W. *Chem. Phys. Lett.* **1988,** *148,* 271-275.

(12) Ostwald, W. *Lehrbuch der Allgemeinen Chem.;* Englemann: Leipzig, 1893; Vol. II-2, p 445.

(13) Turnbull, D.; Fisher, J. C. *J. Chem. Phys.* **1949,** *17,* 71-73.

(14) Dufour, L.; Defay, R. *Thermodynamics of Clouds;* Academic Press: New York, 1963.

(15) Price, F. P.; Gornick, F. *J. Appl. Phys.* **1967,** *38,* 4182-4186.

(16) Butorin, G. T.; Skripov, V. P. *Sov. Phys.—Crystallogr.* (*Engl. Transl.*) **1972,** *17,* 322-326.

(17) Thomson, J. J. *Applications of Chemical Dynamics;* London, 1888.

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technique may make it possible to measure such temperatures directly and thereby to test the consistency of both theories.

Finally, the extreme importance of nucleation, itself, in a wide range of scientific and technological disciplines, makes it of special interest to develop and apply the new technique. It is now possible to investigate nucleation in systems particularly free from contaminants and systems (especially in the case of solid-state transitions) that are virtually impossible to probe on such a time scale by other methods.

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Registry No. CCl_4, 56-23-5; 1,1,1-trichloroethane, 71-55-6; 2,2-dichloropropane, 594-20-7; *tert*-butyl chloride, 507-20-0; selenium hexafluoride, 7783-79-1.

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(18) Reiss, H.; Mirabel, P.; Whetten, R. L. *J. Phys. Chem.* **1988**, *92*, 7241-7246.

Tandem Nucleophilic and Radical Chemistry in the Replacement of the Hydroxyl Group by a Carbon-Carbon Bond. A Concise Synthesis of Showdomycin

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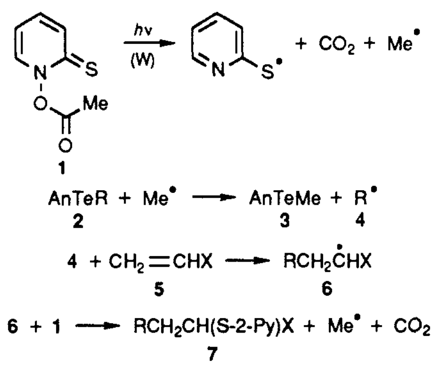
Free-radical reactions have become a popular subject in modern synthetic chemistry.[1] High selectivity and a tolerance for many functional groups make radical reactions easier to carry out than ionic processes. Much elegant radical chemistry has been based on the weakness of the tin-hydrogen bond.[1,2]

In the last six years, we have provided[3] an alternative system for high-yielding reactions, based on acyl derivatives of thiohydroxamic acids. Acyl derivatives of *N*-hydroxy-2-thiopyridone are especially suitable since the reactions are started by tungsten light within a wide temperature range. In addition, on a molar basis, the *N*-hydroxy-2-thiopyridone is at least ten times cheaper than conventional tin reagents.[4]

In this system, the primary source of radicals is the carboxyl function. It would be desirable to adapt the hydroxyl function to the same type of mechanism. There has, indeed, been much interest, especially by Fraser-Reid[5] and Giese,[1,6] for carbohydrate radical chemistry, especially in making the carbon-carbon bond (for other important work, see refs 7 and 8). It seemed to us that the application of organic tellurium chemistry to carbohydrates would permit the generation of a radical at any position where there was a hydroxyl group, and that this could be achieved on the basis of an *N*-hydroxy-2-thiopyridone derivative as light absorber and radical generator. We take advantage of the exceptional nucleophilicity of the anisyl telluride anion and of the exceptional radicophilicity of tellurides in general and of anisyl tellurides in particular.

Scheme I



The hydroxyl group is converted into a suitable leaving group such as mesylate, tosylate, etc. The anisyl telluride anion displaces the leaving group with inversion of configuration, to give an anisyl sugar telluride. Alternatively, an epoxide function can be opened.

Advantage is then taken of facile radical exchange[9] on tellurium(II). However, a "trigger" reaction is needed (Scheme I). The acetyl derivative **1**, on photolysis with tungsten light at room temperature, produces methyl radicals. The methyl radicals react with the telluride **2** to establish a relatively strong Me-Te bond with displacement of the carbohydrate radical **4** (weaker C-Te bond). Radical **4** is a degenerate radical,[10] for by reaction with **2** it regenerates itself. However, as is customary, it is more reactive toward the usual electrophilic olefins than toward the thiocarbonyl of **1**. Hence radical **4** adds to olefin **5** to make a relatively electrophilic radical **6**, which then reacts with the thiocarbonyl function of **1** to afford the product **7** and to re-form the methyl radical and start the cycle again. Methyl anisyl telluride **3** is the other product.

The results summarized in Table I show that the yields are good. After oxidation of the thiopyridine residue in the adduct and the elimination to give trans olefin, a single stereoisomer was obtained in each case.

The occurrence of stereoselective radical reactions with complex molecules can be ascribed to the anomeric effect, the β-bond effect, and steric bulk effects.[1,6] Other recent examples,[11] as well as the work here described, show that very stereoslective radical chemistry can be achieved.

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(1) (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986. (b) Ramaiah, M. *Tetrahedron* **1987**, *43*, 3541. (c) Curran, D. *Synthesis* **1988**, 489 and 665.

(2) Pereyre, M.; Quintard, J. P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987.

(3) (a) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1983**, 939; (b) *Tetrahedron* **1985**, *41*, 3901. (c) Barton, D. H. R.; Zard, S. Z. *Pure Appl. Chem.* **1986**, *58*, 675. (d) Barton, D. H. R.; Ozbalik, N. *Phosphorus, Sulfur Silicon* **1989**, *43*, 349. (e) Crich, D.; Quintero, L. *Chem. Rev.* **1989**, *89*, 1413.

(4) (a) Barton, D. H. R.; Bridon, D.; Fernandez-Picot, I.; Zard, S. Z. *Tetrahedron* **1987**, *43*, 2733. (b) Private communication from Professor M. Newcomb.

(5) (a) Fraser-Reid, B.; Magdzinski, L.; Molino, B. *J. Am. Chem. Soc.* **1984**, *106*, 731. (b) Tsang, R.; Fraser-Reid, B. *Ibid.* **1986**, *108*, 2116; (c) **1986**, *108*, 8102. (d) Tsang, R.; Dickson, J. K., Jr.; Pak, H.; Walton, R.; Fraser-Reid, B. *Ibid.* **1987**, *109*, 3484. (e) Lopez, J. C.; Fraser-Reid, B. *Ibid.* **1989**, *111*, 3450. (f) Lopez, J. C.; Alonso, R.; Frazer-Reid, B. *Ibid.* **1989**, *111*, 6471. (g) Vite, G. D.; Alonso, R.; Fraser-Reid, B. *J. Org. Chem.* **1989**, *54*, 2268. (h) Benko, Z.; Fraser-Reid, B.; Mariano, P. S.; Beckwith, A. L. J. *Ibid.* **1988**, *53*, 2066. (i) Fraser-Reid, B.; Underwood, R.; Osterhout, M.; Grossman, J. A.; Liotta, D. *Ibid.* **1986**, *51*, 2152.

(6) (a) Giese, B.; Dupuis, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 622. (b) Giese, B.; Gonzalez-Gomez, J. A.; Witzel, T. *Ibid.* **1984**, *23*, 69. (c) Giese, B. *Ibid.* **1985**, *24*, 553. (d) Giese, B.; Gronniger, K. *Tetrahedron Lett.* **1984**, *25*, 2743. (e) Dupuis, J.; Giese, B.; Ruegge, D.; Fischer, H.; Korth, H. G.; Sustmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4332.

(7) (a) Rajan Babu, T. V. *Ibid.* **1987**, *109*, 609; (b) **1988**, *53*, 4522. (c) Crich, D.; Ritchie, T. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1461.

(8) (a) Keck, G. E.; Yates, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 5829. (b) Webb, R. R.; Danishefsky, S. *Tetrahedron Lett.* **1983**, *24*, 1357. (c) Keck, G. E.; Enholm, E. J.; Kachensky, D. F. *Ibid.* **1984**, *25*, 1867. (d) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. R. *Tetrahedron* **1985**, *41*, 4079. (e) Keck, G. E.; Kachensky, D. F.; Enholm, E. J. *J. Org. Chem.* **1985**, *50*, 4317.

(9) Barton, D. H. R.; Ozbalik, N.; Sarma, J. C. *Tetrahedron Lett.* **1988**, *29*, 6581.

(10) Delduc, P.; Tailhan, C.; Zard, S. Z. *J. Chem. Soc., Chem. Commun.* **1988**, *308*.

(11) (a) Barton, D. H. R.; Gateau-Olesker, A.; Gero, S. D.; Lacher, B.; Tachdjian, C.; Zard, S. Z. *Ibid.* **1987**, 1790. (b) Barton, D. H. R.; Gero, S. D.; Quiclet-Sire, B.; Samadi, M. *Ibid.* **1988**, 1373; (c) **1989**, 1000; (d) Idem *Tetrahedron Lett.* **1989**, *30*, 4969.

0002-7863/90/1512-891$02.50/0