Matrix Effects in the Infrared Spectra of Cyanoethene (Acrylonitrile) and 2-Chlorobuta-1,3-diene (Chloroprene)

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I.r. spectra of matrix-isolated forms of acrylonitrile and chloroprene are reported. The twisting mode of the vinyl group in the 970—990 cm^{-1} region reveals considerable splitting in each compound which is attributable to high and low energy forms. Measurements are reported on rate of change from high to low energy forms compared between 1 : 500 and 1 : 5 000 dilutions in argon in both compounds at 35 K. The results confirm the low energy form is a polymeric aggregate in the case of acrylonitrile but arises from an intramolecular effect in chloroprene. First-order rate constants were estimated for acrylonitrile and chloroprene at low and high dilutions. Assignments to high and low energy forms are presented between 400 and 3 500 cm^{-1} in each case and the structures of these forms are discussed.

The chemical and physical properties of chloroprene and acrylonitrile are important and relate to their tendency to react readily to form well known polymers and copolymers. The study of i.r. spectra of samples isolated in dilute, low-temperature matrices[1] provides information on molecular vibrations and structure for systems which may not be amenable to examination at normal temperatures and phases because of chemical reactivity or physical perturbation of energy levels.

A rigid low-temperature matrix can maintain a molecule in an unstable high energy state which may relax to a thermodynamically more stable form on annealing the matrix by heating to a temperature at which the matrix softens and permits reorientation to a low energy state. The difference in energy may derive from an energy of interaction within polymeric aggregates, or from a more favourable matrix site or molecular conformation. If the barrier between states is associated with the matrix cage separating adjacent cavities this will be very large at liquid helium temperatures. On heating the matrix the cage barrier will reduce in height to permit some degree of equilibrium to occur. In the case of barriers associated with internal rotation within the molecule Barnes and Whittle[2] have estimated the range of temperatures and barrier heights at which separate conformers can be isolated. Thus two categories of matrix effect can be distinguished in which the low energy state may be associated either with an intermolecular matrix effect or with an intramolecular matrix effect.

Matrix effects appear to be particularly prominent in the region associated with out-of-plane vibrations of the vinyl group. In acrylonitrile[3] matrix effects in this region were described in terms of the existence of monomeric and polymeric or aggregated states resulting from intermolecular changes. In chloroprene[4] similar changes were attributed to conformational or intramolecular changes.

The similarity of effects in these compounds suggests rigorous experimental comparison is merited to distinguish categories of low energy forms. Additionally, it is possible to determine small differences in the fundamental modes of vibration between low and high energy states over the region 400—3 500 cm^{-1}.

Experimental

The sample of acrylonitrile (B.D.H.) and chloroprene (BP Chemicals) were redistilled and dried over $CaSO_4$ and mixed with noble gas (argon or krypton) using vacuum handling techniques which exclude extraneous material as far as possible. Deposition of the samples and recording of spectra were carried out as previously described using an Air Products model CS2L closed cycle liquid helium cryostat and a Perkin-Elmer model 580 spectrophotometer. Calibration using standard gas spectra indicated wavenumber values were accurate to ± 1 cm^{-1}. Samples were deposited on a CsI window, chloroprene in argon was also deposited on a Si window. Using the needle valve to control flow SSO (slow spray-on) spectra were obtained over a period between 4 and 20 h at a rate of between 1 and 6 mmol h^{-1}. Using the pulsing bulb with the needle valve open some 15—25 pulses of sample (10 cm^3; 450 Torr) were applied over *ca.* 45 min. Annealing was carried out using a specially constructed temperature control which allows temperature variation between 8 and 50 K (± 0.2 K). Matrices may be warmed rapidly to predetermined temperatures and maintained at these temperatures to allow accurate and repeatable comparisons of the rate of interconversion of sample from high to low energy forms. Rate constants were estimated from peak height measurements.

Results and Discussion

Matrix Effects and Comparison of Intensities at Different Dilutions.— Intermolecular interactions are reduced by increasing matrix dilution at low temperatures and increased by raising the temperature until mobility of the matrix permits movement between matrix cavities. A study of acrylonitrile restricted to wagging and twisting vibrations of the vinyl group between 950 and 1 000 cm^{-1} revealed conditions[3] under which separation occurred into monomer form (slow spray-on in argon at 1 : 1 000 dilution) and aggregated polymer (annealing of matrix).

The spectrum of chloroprene[4] has closely similar features to those of acrylonitrile in the region 850—1 000 cm^{-1}. Two CH_2 wagging modes are observed in the spectrum of chloroprene corresponding to the two terminal CH_2 groups also with the *trans*-CH=CH or twisting mode at the higher end of this region. The twisting mode has the following remarkably similar features to those in acrylonitrile for which values are shown in parentheses.

(1) A prominent band occurs centred at 975 cm^{-1} in argon (974), 973 cm^{-1} in krypton (972.5), and 975 cm^{-1} in the gas state (971). (2) On annealing the matrix this prominent band disappears in all cases. (3) A weak feature at 983 cm^{-1} in argon (984) and 982 cm^{-1} in krypton (981) intensifies on annealing.

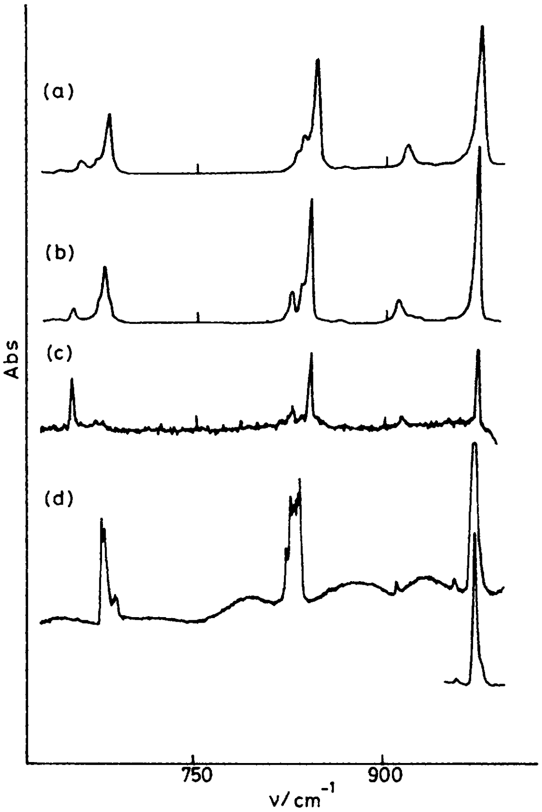

Figure 1. I.r. spectra of chloroprene (850—1 000 cm^{-1}): (a) in krypton 1:1 000 at 8 K; (b) in argon 1:1 000 before annealing at 8 K; (c) in argon 1:1 000 after annealing at 8 K; (d) gas 10 cm path length and 40 Torr (insert 15 Torr) at 298 K

These similarities may suggest the high wavenumber feature in chloroprene is the result of aggregation as shown in the corresponding bands in acrylonitrile. To investigate this possibility careful dilution studies were carried out in argon for 1:100, 1:1 000, 1:5 000, and 1:10 000 over spray-on times of 4 and 20 h in each case. These showed identical intensity ratios for the bands at 983 and 975 cm^{-1} in all cases corresponding to the intensities shown in Figure 1b.

The persistence of the band at 983 cm^{-1} at various dilutions in argon may not preclude assignment to aggregated species. A dilution dependence of intensity in a system in which aggregation takes place implies that the law of mass action controls the reaction and the amount of aggregation increases with the concentration of the monomer in the mixture with argon in the gas phase. Another possibility in a system in which aggregation occurs is that surface or matrix effects control the thermodynamic or kinetic features of aggregation leading to a persistence of aggregation bands at increasing dilution. To investigate surface effect possibilities comparisons were made of spectra isolated on CsI and Si windows. These experiments yielded identical spectra. It was concluded the window material had no effect on the species formed in the matrix. To test the possibility of matrix or other non mass-action effects the following experiment was applied to both chloroprene and acrylonitrile.

Comparison of Time Dependence of Intensity Changes at Different Dilutions.—Two dilutions in argon were selected such that the matrix was neither too concentrated to achieve true matrix separation nor too dilute to achieve adequate signal to noise. Comparison of spectra at 1:500 and 1:5 000 were chosen and spectra of acrylonitrile (Figure 2) and chloroprene (Figure 3) were recorded between 970 and 990 cm^{-1}. The prominent bands in the region 973—975 cm^{-1} assigned to the twist mode of the vinyl group in each compound are isolated by slow spray-on at 8 K. At higher temperatures these bands in both compounds diminish in favour of a high wavenumber band 982—984 cm^{-1} which must correspond to a lower energy state formed by softening or relaxation of the matrix.

If the rate of change from high to low energy form is greater at 1:500 than at 1:5 000 an intermolecular change would be indicated since molecules can come within range of attractive

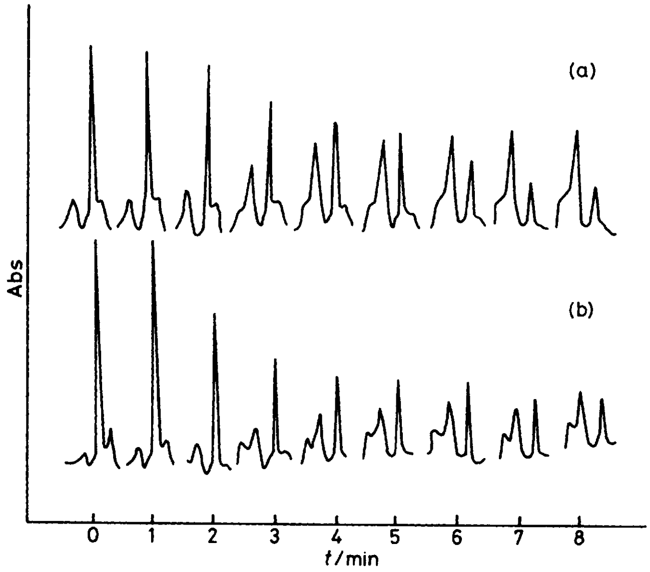

Figure 2. Acrylonitrile (970—990 cm^{-1}) in argon: (a) 1:500 and (b) 1:5 000 at 35 K and different times (t)

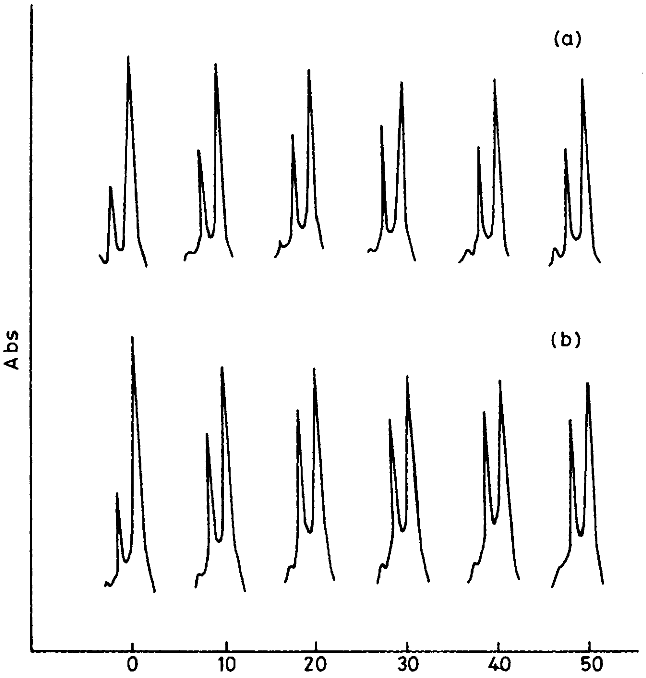

Figure 3. Chloroprene (970—990 cm^{-1}) in argon: (a) 1:500 and (b) 1:5 000 at 35 K and different times (t)

Table 1. I.r. spectra and assignments of acrylonitrile in argon matrix

High energy form			Low energy form	
Wave-number ($\mathrm{cm^{-1}}$)	Relative intensity	Assignments	Wave-number ($\mathrm{cm^{-1}}$)	Relative intensity
		C–H str	3 077	m
		$\mathrm{CH_2}$ sym str	3 044	m
			2 999	vw
2 278	vw		2 282	vw
2 236	m	C≡N str(H)		
		C≡N str(L)	2 234	s
		2 × CH=CH twist(L)	1 959	vw
1 941	vw	2 × CH=CH twist(H)		
1 910	vw			
1 907	m	2 × $\mathrm{CH_2}$ wag	1 907	m
1 905	vw		1 902.5	w
1 623	w			
1 615	w	C=C str(H)		
		C=C str(L)	1 613.5	w
1 596	vw		1 596	vw
1 588	w			
1 430	vw			
			1 417	m (sh)
		$\mathrm{CH_2}$ bend(L)	1 414	vs
1 412	s	$\mathrm{CH_2}$ bend(H)		
			1 364	w
			1 300	vw (sh)
			1 280	w
		$\mathrm{CH_2}$ rock(L)	1 097.5	m
1 092	m	$\mathrm{CH_2}$ rock(H)		
			995.5	w (sh)
			990	m
			985.5	s
		CH=CH twist(L)	983	s
			981.5	m (sh)
974.5	vs	CH=CH twist(H)		
968.5	m		972	w
956	vs		955.5	m
954.5	vs		954.5	vs
953	vs	$\mathrm{CH_2}$ wag	952.5	vs
868	s	C–C str	867.5	w
691.5	s		692	s
683	m			
679	m			

Table 2. I.r. spectra and assignments of chloroprene in argon matrix

High energy form			Low energy form	
Wave-number ($\mathrm{cm^{-1}}$)	Relative intensity	Assignments	Wave-number ($\mathrm{cm^{-1}}$)	Relative intensity
3 122	w	asym $=\mathrm{CH_2}$ str	3 122	w
3 040	w	sym $=\mathrm{CH_2}$ str	3 039	w
1 839.7	vw	2 × $\mathrm{CH_2}$ wag	1 839.3	vw
1 754.5	w	2 × $\mathrm{CH_2}$ wag	1 754.4	w
1 635.1	s	sym C=C str(H)		
		sym C=C str(L)	1 633.9	s
1 591	vw		1 591	vw
1 586.5	vs	asym C=C str	1 586.5	vs
1 397.3	w	sym $\mathrm{CH_2}$ sciss	1 398.7	w
1 361	m	asym $\mathrm{CH_2}$ sciss	1 361.5	m
1 305				
1 291	vw		1 292.2	vw
1 267	vw	C–H bend	1 267	vw
1 260	vw		1 260.8	vw
1 221.9	vs	C–C str(H)		
		C–C str(L)	1 220.9	vs
			1 219.5	vs
1 021.9	m	$=\mathrm{CH_2}$ rock	1 022.3	m
987.8	vw		987.8	vw
		CH=CH twist(L)	982.2	s
975.8	m (sh)			
974.4	s	CH=CH twist(H)		
924.3	vw		924.5	vw
921.8	w		921.6	w
919.6	vs	$=\mathrm{CH_2}$ wag	919.5	vs
911	vw			
			899.4	
896.4	m	$=\mathrm{CH_2}$ rock	895.5	m
			883.8	m
			880.4	m
876	vs	$=\mathrm{CH_2}$ wag	875.9	vs
868	vw			
804.8	vw		804.8	vw
737.2	w	cis wag	737.9	w
698.7	w	C–Cl str	699.2	w
634.6	s	C–Cl str	634.4	s
630.3	(sh)			
523.5	w	skeletal band	523.8	w
410.7	w	C–Cl bend	413	w

interaction more readily in more concentrated matrices. If the two rates of change are the same at different concentrations this would imply an intramolecular change either within the matrix cavity or within the molecule of a kind which is independent of adjacent molecules in adjacent cavities.

Comparisons were achieved by rapidly raising the temperature of the matrix to a value at which appreciable change took place. At 35 K the change from high to low energy form of acrylonitrile took place significantly faster at 1:500 than at 1:5 000 (Figure 2). Rate constants were estimated by assuming the proportions of high and low energy forms were equal to the peak absorbances near 975 and 983 $\mathrm{cm^{-1}}$ respectively divided by their total. The data revealed a better fit for first-order than second-order rate expressions. The correlation coefficient for acrylonitrile being 0.988 at both dilutions, corresponding to first-order rate constants k $(3.4 \pm 0.5) \times 10^{-3}$ and k $(2.3 \pm 0.5) \times 10^{-3}\ \mathrm{s^{-1}}$ at 1:500 and 1:5 000 dilutions respectively. In the case of chloroprene the correlation coefficients were 0.955 in each case corresponding to a rate constant k $(3.5 \pm 1.5) \times 10^{-4}\ \mathrm{s^{-1}}$ at each dilution. This observation is consistent with the dilution experiment and confirms that the low energy form of chloroprene arises from intramolecular rather than intermolecular interactions.

High and Low Energy Forms.—Assignments. An alternative possibility for assignment of the split bands associated with the twisting modes of acrylonitrile and chloroprene would be to a specific effect for that mode such as a Fermi resonance interaction or to an effect localised within a group of the molecule rather than an effect associated with the molecule as a whole. If these changes are correctly attributed to high and low energy forms every other mode will be affected to a greater or lesser extent and it would be remarkable if the twisting mode was unique in achieving sufficient splitting for resolution into separate bands assigned to different states. In order to add weight to the multiple state hypothesis the complete spectra of these states were recorded after maximum separation was achieved using the changes of the twisting mode as a probe to monitor separation.

In the case of acrylonitrile assignments have been reported[5–7] for the solid and vapour states with disagreement only on the relative positions of the twisting and wagging modes. Table 1 reports the assignments of the high energy matrix form (attributed to monomer) and the low energy matrix form (attributed to aggregated polymer). These assignments follow from those in the solid and vapour states. It is noteworthy that the C≡N and C=C stretching modes are shifted by 2 $\mathrm{cm^{-1}}$ to lower value in the polymer whilst the CH_2 bending and rocking modes are increased by 2 and 5 cm^{-1} respectively in the polymer form.

In the case of chloroprene[4] assignments have been reported for a range of physical states. In Table 2 the high and low matrix isolated states are assigned using the shift of 7.8 cm^{-1} between the two twist modes to probe the separation. A shift of 1.2 cm^{-1} is observed between the symmetric C=C stretching modes and of 1.0 cm^{-1} between the two C–C stretching modes. Other small shifts of less than 1.0 cm^{-1} are reported. It is notable that the band centred at 974.4 cm^{-1} in the high energy form has components near 974 and 976 cm^{-1} which respond differently on annealing indicating that the high energy state has some multiplicity.

Structure. Acrylonitriles may be similar to that of acetonitrile which has been shown[8] by far i.r. studies of photochemically produced species to form antiparallel dimers as the low energy state. Statistical calculations[4] for chloroprene in the gas state suggest an equilibrium between a low energy *s-trans* conformation and a high energy *s-cis* conformation separated by 8.2 kJ mol^{-1}.

In the matrix-isolated state the high energy form may also correspond to the *s-cis* conformer. The structure of the band centred at 975 cm^{-1} may also imply one or more non-planar forms. These high energy forms can revert to the *s-trans* conformer if the barrier is reduced, by annealing, to a level which permits thermodynamic equilibria. This tentative explanation is favoured by the similar behaviour of the isolated species in both argon and krypton matrices.

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