Namely, a degree of polymerization of about 40 was deemed to be a minimum unit for leading to the electronic structure characteristic of the neutral PVCz. However, the present cation absorption spectrum is common to all PVCz-n systems including PVCz-4, which indicates that the hole in the polymer is interacting with no more than a few chromophores.

Since there may be configurational and conformational distributions even for PVCz-4, another and more probable explanation is based on the assumption that the positive charge is localized in a dimer cation. This means that the measured spectrum is a superposition of absorption bands of the different dimer cations summarized above, since the spectrum is not identical with that of the sandwich, the second, or the third dimer cation. Although the sandwich and second dimers are responsible for excimer emissions of PVCz,^{12,17} the spectrum of their cations cannot be completely reproduced by the overlap of the bands of the m-DCzPe and r-DCzPe cations. One example of good fitting cases is given in Figure 6, suggesting that a component with absorption above 800 nm should be added. This may be realized only by considering the contribution of the DCzB cation, but the combination of the latter cation with the r-DCzPe or the m-DCzPe cation does not give the simulated spectrum similar to the measured one. Therefore, it is considered that three different dimer cations are involved and their statistical average constitutes the spectrum of the polymer cation. The formation of sandwich and second dimer sites is characteristic of PVCz and has been confirmed by fluorescence and NMR data,^{12,18} while the importance of another geometrical structure of two carbazolyl groups whose model is DCzB is demonstrated here for the first time.

In contrast with the above results on polymer cations, anion radicals of the present polymer and model compounds give the same absorption spectrum as that of the monomer anion. The electron transferred to these compounds is stabilized as a monomer anion and no interaction between the anion and the neutral chromophore was observed even in the polymer.

Summary

On the basis of transient absorption spectra, it is concluded that the hole (or electron) in the polymer is trapped as some dimer cations (or monomer anion) and not delocalized over chromophores. The statistical average contribution of the three kinds of dimer cation determines the absorption spectrum of polymer cations which is ascribed to the configurational and conformational structures of polymers in solution.

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Registry No. PVCz-n, 25067-59-8; PCzEVE-n, 53807-87-7; PU-I-n, 77090-85-8; PU-II-n, 77090-86-9; EtCz, 86-28-2; DCzP, 25837-66-5; DCzB, 1484-96-4; (*trans*-9,9'-(1,2-cyclobutanediyl)dicarbazole-3,3'-dimethanol)·(hexamethyleneisocyanate) (copolymer), 77110-00-0; (*trans*-9,9'-(1,2-cyclobutanediyl)dicarbazole-3,3'-dimethanol)·(*m*-phenylenedimethyleneisocyanate) (copolymer), 79675-91-5.

Picosecond Kinetics by Exchange Broadening in the Infrared and Raman. 3. CH₃CN·IBr

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Spectra of the ν_2 and $\nu_3 + \nu_4$ bands of CH₃CN in the presence of IBr and in CCl₄ solution were measured over a range of temperatures. The spectra could be analyzed to reveal the kinetics of the CH₃CN + IBr \rightleftharpoons CH₃CN·IBr reaction, in the picosecond range. Association and dissociation rate constants were determined and, from them, activation energies and entropies.

Some time ago we reported on the reaction between IBr and benzene in an inert solvent.¹ The kinetics of that reaction became apparent through its effect on the line shape of the IBr vibrational band. At low temperatures two bands, one corresponding to the vibration of IBr bound to benzene (forming a charge transfer complex) and one corresponding to free IBr, are observed. As the temperature is raised these two bands broaden and coalesce in much the same way as that observed for exchange reactions in NMR and ESR. In this way it is possible to study reactions in the picosecond range (1 cm⁻¹ corresponds to 5×10^{-12} s) for ground-state molecules by a simple technique.

The spectral region in which the IBr vibration occurs, 230–280 cm^{-1} , is, however, an inconvenient one. The benzene spectrum, on the other hand, is too rich for a convenient, reasonably well-separated band to be found that will lend itself to a kinetic study. The simplest solution, therefore, to the problem of finding a suitable test case for the study of charge transfer complex association–dissociation kinetics was to change the donor. It was found that acetonitrile forms a complex with IBr the association–dis-

sociation kinetics of which are in the picosecond range and that the spectrum of this molecule includes bands suitable for our purpose and in a convenient spectral range.

Spectra were taken on a Perkin-Elmer 225 infrared spectrometer with a resolution of 0.6–0.7 cm⁻¹. Samples were contained in a RIIC variable-temperature cell. The temperature range in this study was –5 to +40 °C. Acetonitrile was purified by reflux over P₂O₅, treatment with NaHCO₃, and subsequent distillation. Acetonitrile and IBr were dissolved in CCl₄ at concentrations of 0.1 to 0.4 M for IBr and 0.1 to 0.2 M for CH₃CN. Fresh solutions were always used to avoid formation of products resulting from slow reactions between the reactants. The optical path was 1 mm. Results are reported as absorbances.

Spectra of the ν_2 and $\nu_3 + \nu_4$ bands of acetonitrile in CCl₄ solution and in the presence of IBr are reproduced in Figures 1 and 2. The ν_2 band at 2253 cm⁻¹ was chosen for study, because it involves the CN vibration which should be affected the most by complexation, since it is the CN group which is responsible for the formation of the complex with IBr. The $\nu_3 + \nu_4$ combination band at 2289 cm⁻¹ contains the C-C stretch ν_4 (ν_3 is a CH₃ deformation) which should also be affected by complexation and

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TADIEI.	NT- 41	and Tak	1 Mildala a	nd Data	Constant
TABLE I	Natural	and lot	al widths a	na kate	Constant

				$\Delta \nu_{1/2}$, σ cm ⁻¹						
	[IBr], ^a T, °C M	$[CH, CN]^{a}$	free		bound		app first-order rate constant. ^c	second-order rate constant. ^c	rate constant. ^d	
		M	M	natural	total	natural	total	s ⁻¹	M ⁻¹ s ⁻¹	s ⁻¹
	+20	0.1	0.1	5.6	6.4	3.6	8.4	1.5×10^{11}		9.05 × 10 ¹¹
	+20	0.2	0.1	5.6	7.2	3.6	8.4	3.0×10^{11}	1.68×10^{12}	9.05×10^{11}
	+20	0.3	0.2	5.6	8.0	3.6	8.4	$4.5 imes 10^{11}$		9.05×10^{11}
	+20	0.4	0.1	5.6	8.8	3.6	8.4	6.0×10^{11}		9.05×10^{11}
	-5	0.3	0.2	4.8	6.4	2.8	5.0	3.0×10^{11}	1.43×10^{12}	4.14×10^{11}
	+40	0.34	0.2	6.4	9.2	4.8	12.4	5.3×10^{11}	1.83×10^{12}	1.43×10^{12}

^a Overall concentrations. ^b Widths are half-width at half-height. ^c Formation. ^d Dissociation.



Figure 1. Spectra of the v_2 and $v_3 + v_4$ bands of CH₃ CN in CCl₄ solution in the presence of IBr. [IBr] = 0.3 M, [CH₃CN] = 0.2 M. Optical path 1 mm.

it lies conveniently close to v_2 . It was included in our study to provide a check on the results obtained from the analysis of v_2 .

The spectra shown in Figure 1 differ from one another in temperature, those in Figure 2 in concentration. This means that not only line shapes change but also the relative intensities of the bands due to free and bound CH₃CN. On some of the spectra two distinct peaks can be observed for a given band, on others shoulders only, and in other cases the two peaks have coalesced beyond separation. For both ν_2 and $\nu_3 + \nu_4$ the frequency of bound CH₃CN is higher than that of free CH₃CN. The spectra were analyzed with the modified Bloch equations as outlined in the first article of this series.² For the analysis of either the ν_2 or ν_3 + ν_4 band seven parameters are required: two peak positions, two natural widths, two lifetimes, and the ratio of intensity coefficients of free and bound CH₃CN. For each band the peak position and natural width for free CH₃CN could be determined independently and the lifetimes are, of course, related through the known equilibrium constant.⁵ In the case of ν_2 the peak position of bound CH_3CN could be obtained from the spectrum at -5 °C where the bands are sufficiently separated to be fitted by Lorentzians. This left us then with three parameters (natural width of bound CH₃CN, one lifetime, and ratio of intensity coefficients) to adjust so as to obtain the best fit of calculated to observed spectra. An example of such a fit is shown in Figure 1. For $v_3 + v_4$ the peak



Figure 2. Spectra of the ν_2 and $\nu_3 + \nu_4$ bands of CH₃CN in CCl₄ solution in the presence of IBr: (A) +20 °C, [IBr] = 0.1 M, [CH₃CN] = 0.1 M; (B) + 20 °C, [IBr] = 0.2 M, [CH₃CN] = 0.1 M; (C) +20 °C, [IBr] = 0.3 M, [CH₃CN] = 0.2 M; (D) +20 °C, [IBr] = 0.4 M, [CH₃CN] = 0.1 M; optical path 1.0 mm.

position of bound CH₃CN could not be obtained independently. We therefore used in the analysis the lifetime obtained from the v_2 analysis as well as the natural widths for bound CH₃CN (on the assumption that these are determined primarily by the increased moment of inertia of the complex and are therefore similar in both cases). In this way only two adjustable parameters were left (one peak position and ratio of intensity coefficients). In this way the $v_3 + v_4$ results could be used to corroborate the findings obtained from the v_2 band though their analysis does not provide an independent determination of lifetimes.

The natural widths for both bound and free CH₃CN were found to be temperature dependent as observed by Yarwood for the latter.³ As might be expected the natural widths of bound, slower moving, acetonitrile are smaller than those of free acetonitrile. The kinetic broadenings from which rate constants are calculated (through $k = 2\pi\Delta\nu_{1/2}$) were then taken, as in part 1,² as the broadening over and above the natural width. Natural widths, total widths, and rate constants calculated therefrom are collected in Table I.

Unlike our previous studies^{2,4} which were concerned with first-order reactions, the present case involves a second-order

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Figure 3. Plot of the apparent first-order association rate constant vs. free IBr concentration at 20 °C.

 TABLE II: Activation Energies and Entropies and Thermodynamic Functions

E_{a}^{a} , cal/mol	$\Delta S^{\pm},^{a}$ eu	$\Delta H, b$ cal/mol	$\Delta S,^b$ eu
formation 890 ± 50 dissociation 4640 ± 100	-1.6 ± 0.7 9.9 ± 0.7	-4100 ± 300	-12.8 ± 0.9

^a This work. Uncertainties quoted are standard deviations determined from the experimental scatter. ^b Formation. Literature values. Reference 5.

reaction and concentration effects should be evident. The lifetime or kinetic broadening of free CH₃CN, or the apparent first-order rate constant for complex formation, should depend on the concentration of free IBr. In Figure 3 the dependence of the apparent first-order rate constant at 20 °C on free IBr concentration is shown. Free IBr concentrations were calculated with the equilibrium constant (in CCl₄) available from the literature.⁵ The slope of the straight line obtained obviously yields the second-order association rate constant. These rate constants are also collected in Table I.

Clearly the values of the second-order rate constants we report are much higher than that of a diffusion-controlled rate constant. The diffusion-controlled value, however, is derived for dilute solutions and for times longer than 10^{-11} s (with transient effects persisting to 10^{-7} s).⁶ Now our solutions are fairly concentrated—in a sphere of radius 16 Å around a CH₃CN



Figure 4. Plots of $\ln k$ vs. 1/T for the formation (\bullet) and dissociation (\Box) rate constants.

molecule there will be, on the average, one IBr molecule at 0.1 M IBr concentration, the radius decreasing to ~ 10 Å at 0.4 M. With a reaction distance of probably 5–7 Å (it is 4.3 Å for I + I in CCl₄,⁶ both IBr and CH₃CN are polar, the dipole of the latter being 3.9 D) this means that, assuming random distribution, the reactants are never far apart. But the distribution will not be quite random. It will be affected by cage effects around dissociating complexes, keeping reactants closer to one another with their successive encounters within the cage counting as distinct events on a picosecond scale. Indeed, rate constants for formation of charge-transfer complexes of the same order of magnitude as ours have been reported before (from dielectric relaxation measurements).⁷

In Figure 4 plots of ln k vs. 1/T are reproduced. From these activation energies are obtained. Also, calculating ΔG^* from $k_r = (kT/h) \exp(-\Delta G^*/RT)$ and plotting it vs. T one obtains straight lines from the slopes of which values of ΔS^* can be calculated. The values we obtained are collected in Table II along with literature values for ΔH and ΔS .

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Registry No. CH₃CN, 75-05-8; IBr, 59372-45-1; CH₃CN·IBr, 90351-37-4.

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