Figure 4 shows a plot of the glass transition temperatures from tan δ data *versus* wt% nitrile rubber. It is clear that there is not a simple linear relation between the glass transition temperature and composition. It must, however, be kept in mind that some of the tetramethylene terephthalate segments are involved in crystallites, and, hence, are not available to mix with the nitrile rubber. If the data are replotted assuming that only the poly(tetramethylene ether) glycol terephthalate segments, which are present in the polyether ester at a level of about 50 wt%, are available for blending, it is found that the data points lie much closer to the straight line joining the glass transition temperatures of the constituent polymers. However, as the polyether ester transition at -32°C is assigned[16] to the poly(tetramethylene ether) glycol terephthalate segments, it is clear from *Figures* 1 and 3 that all these segments are not blended with the nitrile rubber.

Taken together these observations indicate that there is some mixing of the polyether ester and the nitrile rubber. At high levels of polyether ester it is likely that a significant fraction of the tetramethylene terephthalate segments crystallize, but some of the poly(tetramethylene ether) glycol terephthalate segments do mix with the nitrile rubber in all three blends. However, it is not clear at any of the polyether ester concentrations if any of the amorphous tetramethylene terephthalate segments mix with the nitrile rubber.

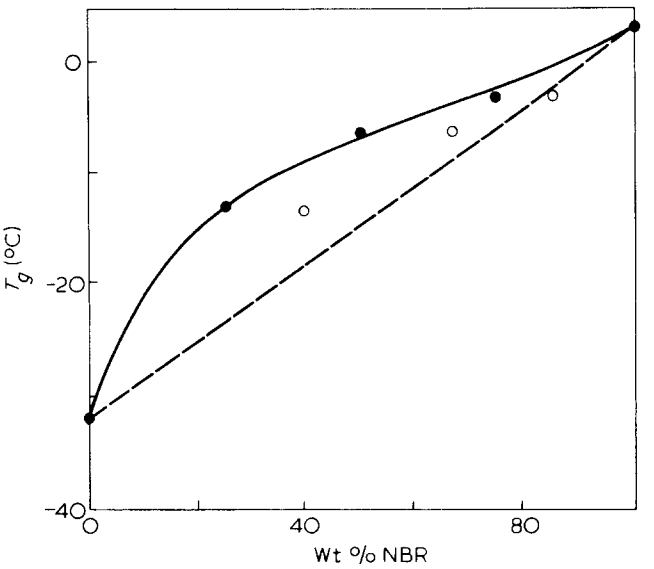

Figure 4 Glass transition temperatures (T_g) of the constituent polymers and the blends *versus* wt % nitrile rubber. The symbol (○) refers to the case where only the poly(tetramethylene ether) glycol terephthalate segments are considered

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Charge transfer complex between maleic anhydride and pyridine

J. A. Chamizo*, G. Mendoza-Díaz and J. L. Gázquez
Facultad de Quimica, Universidad Nacional Autónoma de México, Ciudad Universitaria, Mexico 20, D.F.

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Charge transfer complexes (*CTC*) play an important role in the understanding of many chemical phenomena, such as hormone action[1], carcinogenic activity[2], and solvent–solute interactions[3]. Recent work has proved that they appear as intermediates in various organic reactions[4].

In a recent publication Wurm, Regel and Hallensleben[5] (WRH) discuss the formation of a 2:1 maleic anhydride (MAH):pyridine (Py) compound as a polymerization reaction intermediate. Their first step in this mechanism is the formation of a *CTC* between one molecule of Py and one of MAH. The purpose of the present work is to show, from a theoretical calculations, that there is a more stable configuration[6] than the one proposed by WRH.

The calculations were performed within a modified *CNDO* version[7] of the all-valence electron *SCF–MO* approach. The method has been employed in previous successful investigations of catalytic systems because the parametrization has been designed to treat large distance molecular interactions. In particular, good results have been obtained for charge transfer and bond order[8].

The first step consisted of the evaluation of the charge distribution, the ionization potential and the electron affinity of the isolated molecules[9]. These results together with the values of the *LEMO* and *HOMO* predict that Py acts like an acceptor and MAH acts like a donor of charge (see *Table* 1).

To evaluate the equilibrium distance, the charge transferred and the charge distribution in the molecules of the *CTC* we have allowed MAH to approach Py in two different ways, keeping both molecules rigid (see *Figure* 1). Notice that path A corresponds to the one proposed by WRH and that the charge distribution is slightly different.

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Table 1 Results for the isolated molecules

Molecule	*HOMO*[a]	*LEMO*[a]	ΔE_{H-L}	*IP*[b]	*EA*[b]
MAH	−8.265	+3.291	11.556	10.33	4.81
Py	−6.686	+5.203	11.889	8.1	7.1

[a] All energies in eV. *HOMO* (highest occupied molecular orbital), *LEMO* (lowest empty molecular orbital)
[b] Values of the ionization potential (*IP*) and electron affinity (*EA*) were calculated in vertical form

Table 2 Comparison between paths A and B[a]

CTC	Molecule	Equilibrium distance (Å)	Charge transfer	Stabilization energy (eV)
MAH–Py (A)	MAH Py	2.1	−0.1137 +0.1137	2.68
MAH–Py (B)	MAH Py	1.85	−0.281 +0.281	12.38

[a] See *Figure 1*

However, we can see from the results obtained (*Table* 2) that path B represents a more stable *CTC*, in agreement with the idea[10] that the amount of charge transferred is greatest for the most stable complex.

It is well know that the CNDO method overestimates stabilization energies and gives rather small values for equilibrium distances, nevertheless the correct tendency was found, namely, MAH acting as an acceptor and Py acting as a donor, Thus, we believe that the results obtained are reliable, not in an absolute value sense but as the right trend.

Acknowledgements

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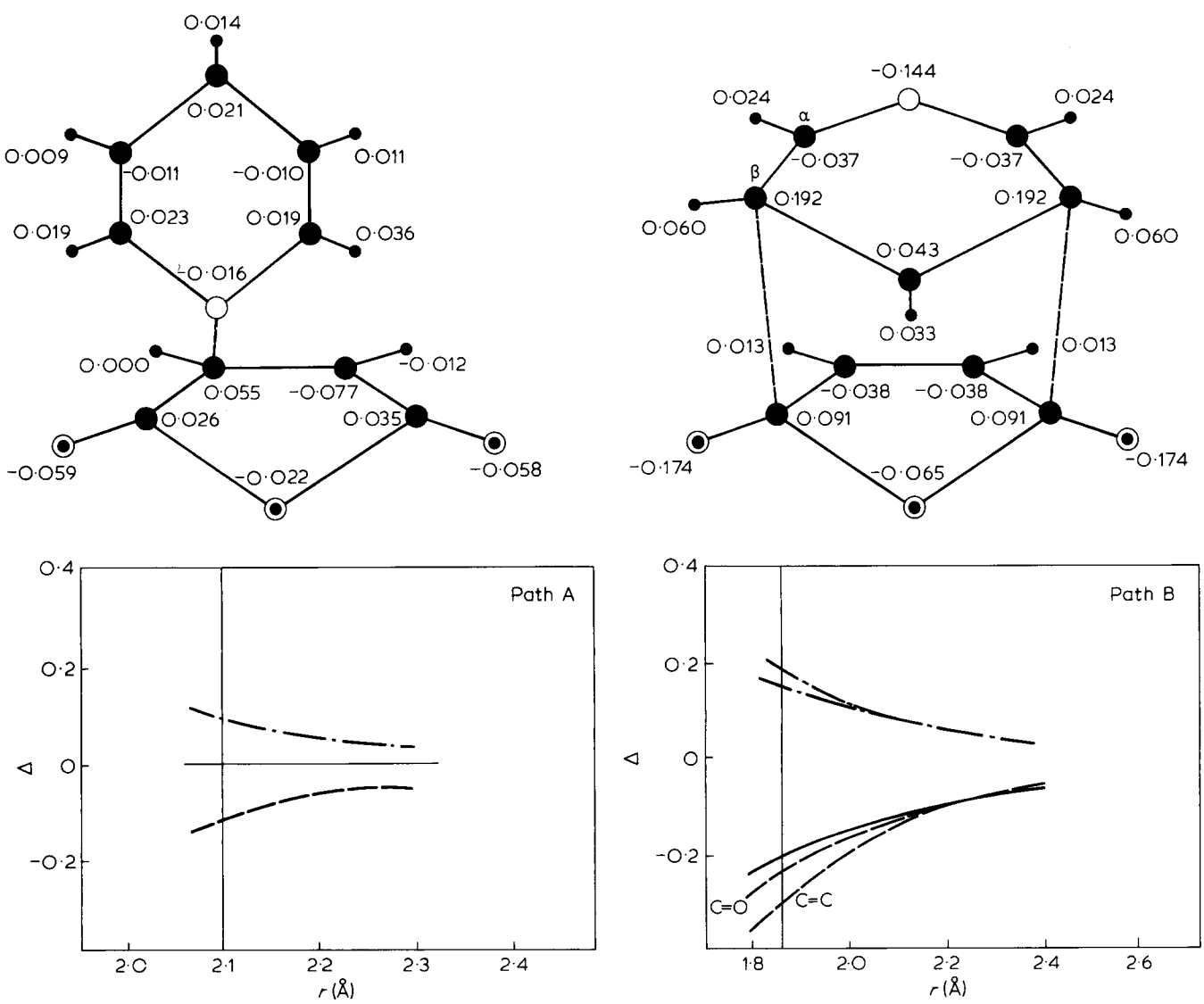

Figure 1 Variation of the bond order that had the greatest change in the *CTC* formation *versus* the intermolecular distance. Δ is the difference between the bond order in the *CTC* and the same bond order in the isolated molecule. This corresponds to the C=C in MA and the C–N in Py in Path A and to the C=C and C=O in AM and the C_α–C_β in Py. Numbers in the molecular diagram are the difference between the atomic charge in the *CTC* and the atomic charge in the isolated molecule. – – –, MAH; ——, Py; —·—·—, *CTC*: ● carbon, ○ nitrogen, ◉ oxygen, ● hydrogen

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Mechanism of thermal decomposition of poly(vinylidene chloride)

Alberto Ballistreri, Salvatore Foti, Pietro Maravigna, Giorgio Montaudo and Emilio Scamporrino

Istituto Dipartimentale di Chimica Industriale dell' Universitá di Catania, Viale A. Doria, 6 95125 *Catania, Italy*

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The thermal decomposition of poly(vinyl chloride) (PVC) and poly(vinylidene chloride) (PVdC) proceed through an endothermic dehydrochlorination reaction[1], but little information exists in the literature on the mechanism of thermal decomposition of PVdC, which is assumed to be similar to that of PVC[2-4].

We have previously found[5] that direct pyrolysis in the ion source of a mass spectrometer (m.s.) can provide useful information on the volatile species evolved during the thermal decomposition of polymeric materials and so give an insight into the thermal decomposition mechanism. We have used this technique in order to detect the volatile decomposition products formed by heating PVdC. Pyrolyses were carried out in quartz probes using the direct insertion inlet of an electron impact mass spectrometer LKB-9000S following the technique described elsewhere[5].

The experimental conditions were as follows: electron energy, 18 eV; ion source temperature, 250°C; accelerating voltage, 3.5 kV; heating rate 10°C min^{-1}.

Figure 1 shows the mass spectrum relating to the pyrolysate of PVdC at 190°C. Fragments at $m/e = 36$ (HCl), 96 ($C_2H_2Cl_2$), 180 ($C_6H_3Cl_3$), 264 ($C_{10}H_4Cl_4$), are the most abundant. These species are highly informative in accounting for the decomposition mechanism of PVdC.

Following the general trend of 1,1-disubstituted vinyl-polymers, PVdC tends to unzip to form monomer when heated, but the unzipping rate is greatly reduced by the concomitant dehydro-chlorination reaction, leading to the formation of linear chlorinated polyene structures (*Scheme* 1). The latter decompose and rearrange intramolecularly to produce aromatic compounds such as trichlorobenzene and tetrachloronaphthalene. This process occurs in parallel with an extensive crosslinking reaction which yields char[6].

Further support to this reaction scheme comes from the effect of ZnO on the thermal decomposition of PVdC.

Figure 2 shows the volatilization rate profiles (absolute ion intensity vs. temperature) of the thermal degradation products of pure PVdC (*Figure* 2*a*) and PVdC/ZnO (10 wt %) mixtures (*Figure* 2*b*).

As a result of the presence of ZnO, the thermal decomposition of PVdC occurs at a considerably lower temperature, whereas $ZnCl_2$ appears among the volatile pyrolysis products.

Evidently, $ZnCl_2$ is produced in the early stages of the thermal decomposition by reaction of ZnO with the HCl

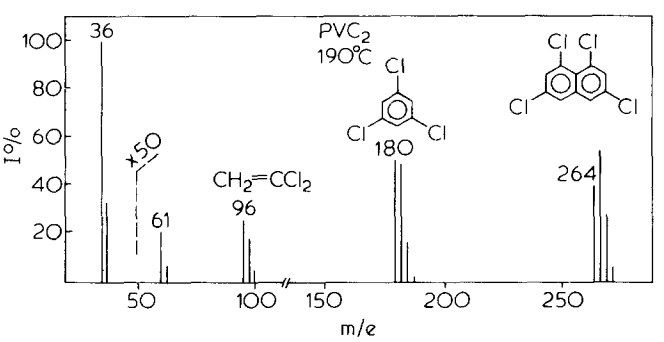

Figure 1 Mass spectrum (18 eV) of the products of thermal degradation for PVdC at 190°C

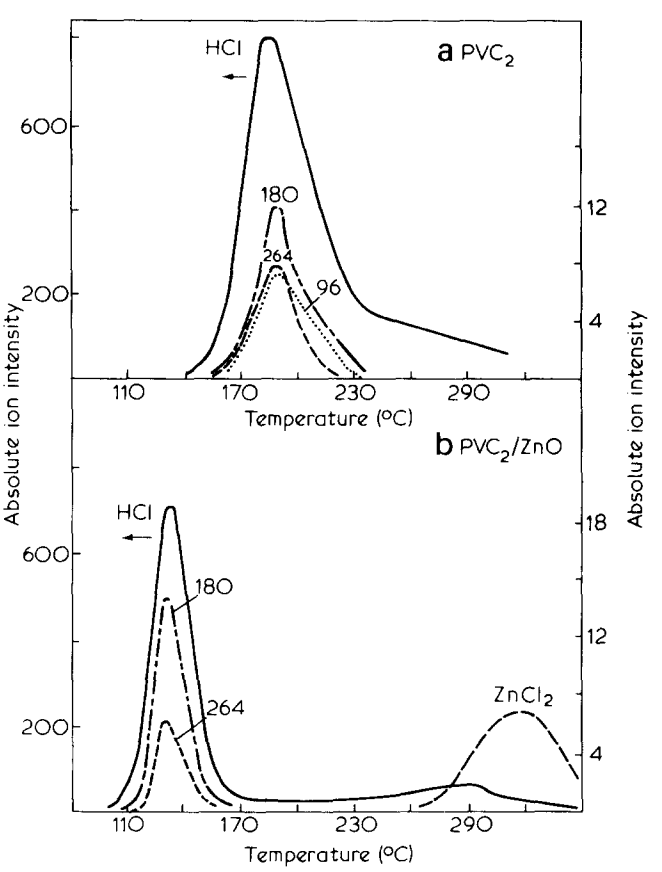

Figure 2 Absolute ion intensity of relevant mass peaks (m/e = 96, vinylidene chloride; m/e = 180, trichlorobenzene; m/e = 264, tetrachloronaphthalene) as a function of the temperature for: (a) PVdC; (b) PVdC/ZnO (10 wt %) mixture

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