

Thermal degradation of poly(vinyl chloride) in oxidative and non-oxidative atmospheres

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(Received 3 October 1983)

The thermal degradation of PVC has been studied. The formation of benzene and crosslinkages are closely correlated, and the critical temperature of the benzene evolution is found to be about 583 K. Thermodynamic functions have been estimated from the specific reaction rate of benzene formation, and the mechanism of cyclization is discussed.

(Keywords: PVC; pyrolysis; cyclization; reaction rate; cross-linking; dehydrochlorination)

INTRODUCTION

Despite the fact that poly(vinyl chloride) (PVC) has poor thermal stability, its ease of processability and versatile applicability gives it an important position among the general purpose plastics.

A number of works on the thermal degradation of PVC at processing temperatures of around 433–523 K have shown^{1–4}: (1) primary HCl loss and polyene formation are similar processes in the presence or absence of oxygen; (2) the polyene sequences are oxidized in a fast radical reaction; (3) the peroxy product formed decomposes rapidly; (4) the radicals formed during the oxidation of polyenes or the degradation of peroxides attack the intact monomeric units and initiate further HCl evolution.

In our previous work⁵ we studied the dielectric absorption caused by the molecular relaxation of PVC decomposed thermally in air, and it was reported that, as the thermal degradation proceeds, the magnitude of dielectric absorption changes in three stages: (1) the formation of polyene sequences, (2) the oxidation of polyene sequences, (3) the formation of crosslinks.

At higher temperature it has been well known that PVC evolves hydrogen chloride and other volatile degraded products in both inert and oxidative atmospheres^{6–8}, and that the most abundant organic pyrolyzate was benzene^{9–11}. Furthermore, Lattimer *et al.*¹² pointed out that the formation of volatile organic pyrolyzates in PVC is essentially a non-oxidative process, and that under flaming conditions organic pyrolyzates are converted to oxidized products (mostly CO, CO₂ and H₂O), but under non-flaming conditions there is little evidence for the formation of hydrocarbons containing oxygen. O'Mara¹³ and other authors^{12,14,15} showed that benzene is formed by an intramolecular path during the high temperature pyrolysis and a Diels–Alder type condensation between neighbouring polyenes was proposed to account for the

crosslinking that takes place early in the decomposition. The different mechanisms for the formation of benzene at temperature ranges below and above the temperature corresponding to the completion of dehydrochlorination were not understood.

The object of this study was to obtain evidence for the path of benzene formation during the thermal degradation of PVC in both oxidative and non-oxidative atmospheres by means of measurements of rates of benzene evolution at various temperatures.

EXPERIMENTAL

Materials

The PVC used in this work, Geon 103 EP (Nippon Geon Co. Ltd.) had a viscosity-average degree of polymerization of 1050. No additives were added to the PVC samples. The mean value of agglomerated particle size was 136 μm . Inter and intra particle void volume (determined by mercury porosimetry using a Aminco–Winslow porosimeter) were 0.70 ml/g and 0.23 ml/g, respectively. All reagents used in this investigation were of analytical grade and were used without further purification.

Method

A gas chromatograph (model 4APTF PYP-1A Shimadzu Co., Ltd.) was employed to estimate the amount of benzene and related gaseous products evolved. Benzene was used as a standard in the calibration of the gas chromatographic peak height. The gas chromatographic circuit was of metal tubing and was maintained at 70°C. Helium as carrier gas was passed with a flow rate of 60 ml min⁻¹ at a pressure of 1 kg cm⁻². A small quantity of the sample PVC (about 10 mg) was loaded in the small platinum boat. The PVC was pyrolysed in a specially designed

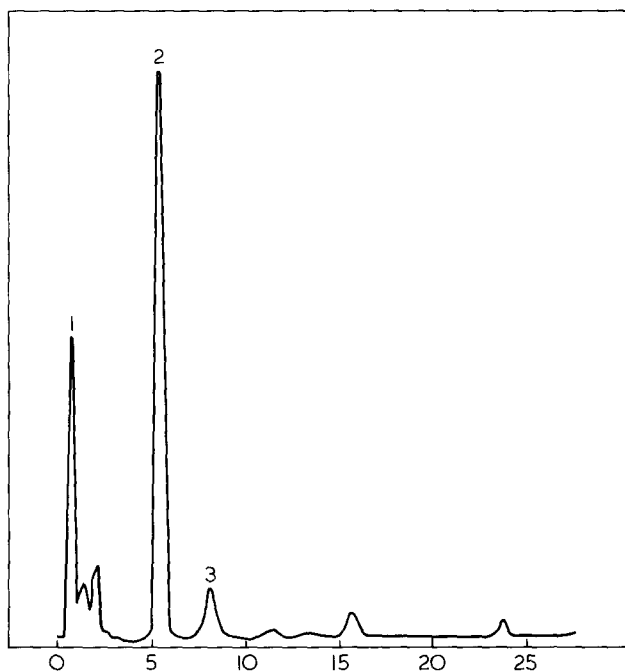


Figure 1 Typical pyrogram obtained at 753 K of PVC in air

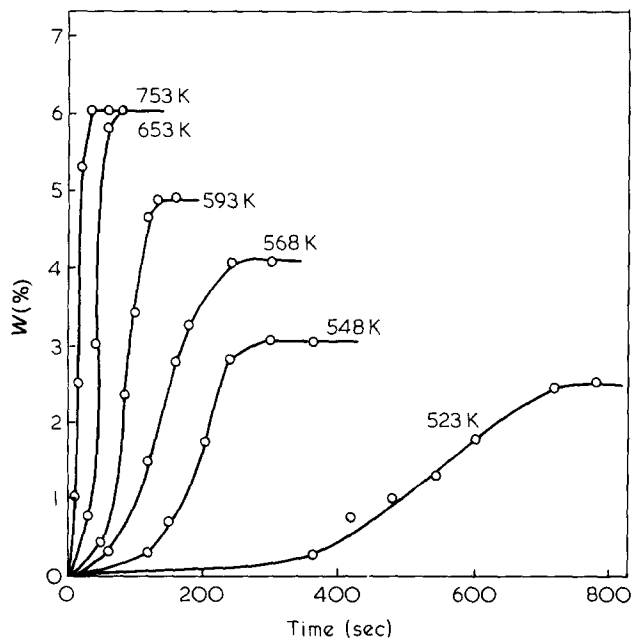


Figure 2 Released benzene as weight fraction of PVC in air

furnace at temperatures from 523 to 753 K and the weight of benzene evolved was determined gas chromatographically as weight per cent of the original PVC sample.

Swelling measurements were carried out for the determination of the average molecular weight of inter-chain linkages (M_c) of the degraded PVC. The samples were rapidly chilled in a refrigerator (about 4°C), and then immersed in the swelling agent (cyclohexanone at 30°C ± 0.1°C). Equilibrium swelling was attained within ten days for all cases examined. The swollen samples were weighed 10 min after complete wiping with filter papers.

An infra-red spectrophotometer Type IR-G (Nippon Bunko Co. Ltd.) was used for further analysis of solid degraded residues of PVC. All the i.r.-measurements were done by the KBr method. In order to prepare the tablets, the degraded residues were swollen with tetrahydrofuran

(THF), and exhaustively dried at room temperature for several days.

RESULTS AND DISCUSSION

Preliminary measurements of equilibrium swelling showed that the original PVC sample did not have any crosslinks.

The volatile pyrolyzates analysed gas chromatographically which were similar to those reported previously¹⁶⁻²⁰ are shown in Figure 1 (where peak number 1, 2 and 3 denote the aliphatic hydrocarbon, benzene and toluene, respectively). The weight fraction of benzene, w , is plotted against the reaction time in Figure 2 for air and in Figure 3 for helium atmospheres. The evolved benzene was found to increase with the reaction time and to attain an equilibrium value. Moreover, it was also observed that at temperatures below 593 K the equilibrium values are larger in air than in helium, and that at higher temperatures, 593 K, however, the ambient atmosphere had little influence on the benzene evolution. Further, in the region above 653 K nearly the same values of equilibrium amounts of evolved benzene in both air and helium are observed (about 6 wt% for the original PVC).

To clarify the temperature dependence of benzene, the reaction time corresponding to the critical point of each curve in Figures 2 and 3 was plotted against the pyrolysis temperature in Figure 4. The fact that the plot exhibits an inflection point at about 583 K seems to suggest a change in mechanism of benzene evolution.

In order to elucidate the further details of degraded residues containing benzene derivatives, i.r.-measurements were carried out for samples degraded to different degrees. Although absorption bands of benzene derivatives are observed at 1600 and 750 cm^{-1} , in comparing the quantity of Cl with that of benzene derivatives, both the absorptions at 750 cm^{-1} and 690 cm^{-1} (the stretching vibration of C-Cl) were measured and are shown in Figures 5 and 6.

In the lower temperature region, the intensity of the absorption band 750 cm^{-1} at 548 K is found to increase

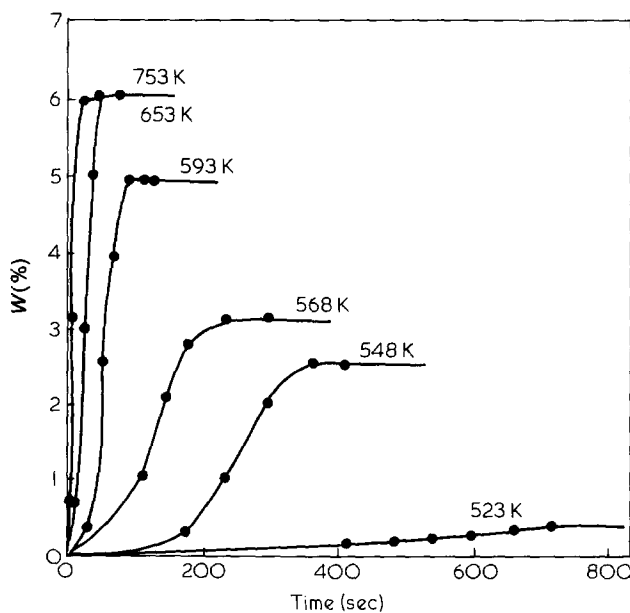


Figure 3 Released benzene as weight fraction of PVC in helium

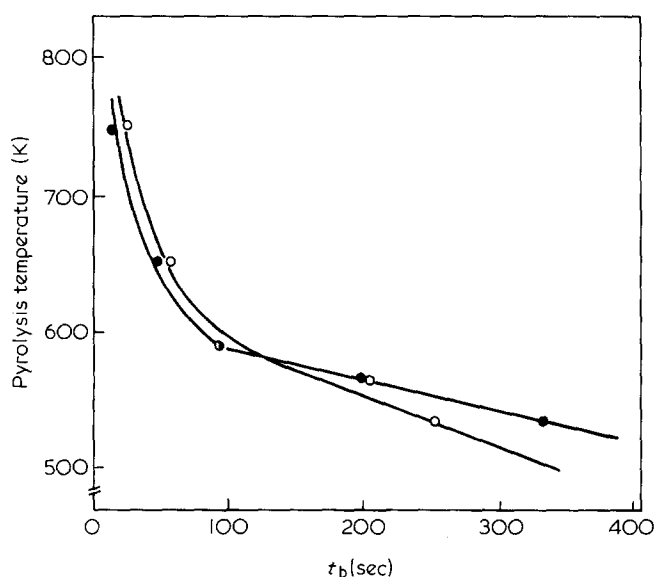


Figure 4 Relationship between pyrolysis temperature and critical time for benzene evolution degraded (O) in air and (●) helium

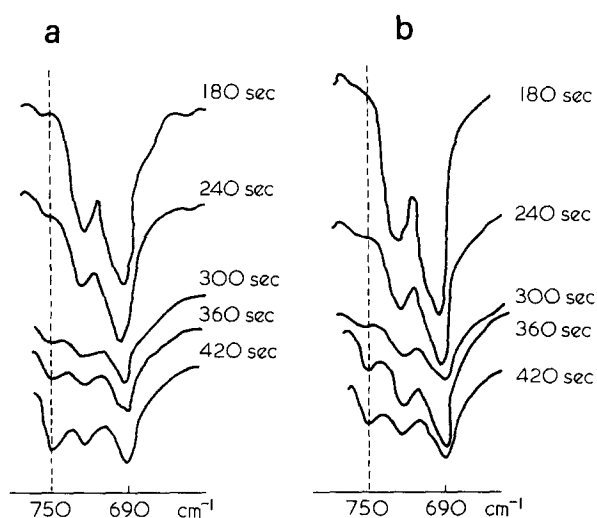


Figure 5 Infra-red spectra of PVC thermally degraded at 548 K (a) in air and (b) helium

apparently with the reaction time. On the other hand, in the higher temperature region, at 753 K, the benzene derivatives (750 cm^{-1}) are found to increase rapidly, while the intensity of the 690 cm^{-1} band (C-Cl) decreases with the reaction time and finally diminishes to zero. This fact seems to indicate that even after the evolved benzene attained a constant value, aromatic derivatives, which presumably correspond to polycyclic networks, increase in degraded residues, and therefore support the result reported by Shimokawa *et al.*²¹

In order to elucidate the effect of other secondary reactions, such as crosslinking, on the formation of benzene, the average molecular weight between successive linkages (M_c) in degraded solid products of PVC was estimated according to the following Flory and Rehner's equations²²,

$$v_2 = \frac{1}{1 + \{(\rho_2/\rho_1)[(W_b/W_a) - 1]\}} \quad (1)$$

$$M_c = \frac{\rho_2 V v_2^{1/3}}{-\ln(1 - v_2) - v_2 - \mu v_2^2} \quad (2)$$

where v_2 is volume fraction of crosslinked polymer in equilibrium swollen condition with solvents; W_a and W_b are the sample weights before and after swelling; ρ_1 and ρ_2 the densities of solvent and unswollen residues. μ in equation (2) is a thermodynamic non-ideality parameter representing a certain interaction between polymer and solvent, and is assumed here to be 0.41 for the system of PVC-cyclohexanone²³. V is the molecular volume of the solvent at 30°C .

Values of M_c are plotted against reaction time (Figure 7) show that M_c decreased with reaction time and finally approached a constant value of about 230, irrespective of the ambient atmosphere. Since the PVC residues resulting from thermal degradation at the lower temperature region involved large amounts of solvent-soluble components, the exact value of M_c could not be determined at temperatures below 523 K. The crosslinking reaction is considered to proceed until M_c attains about 230. The critical reaction time related to the equilibrium value of M_c , t_m , and the other critical reaction time related to the equilibrium value of evolved benzene, t_b , (as shown in Figures 2 and 3) are summarized in Table 1. It is clear that t_m and t_b are closely correlated to each other.

The specific rate of reaction, k , was assumed to be

$$k = w/(t_b - \tau) \quad (3)$$

where τ denotes the induction period of benzene evolution, which corresponds to the inflexion point of each curve in Figures 2 and 3. The specific reaction rates obtained are listed in Table 2, and are plotted against $1/T$, as an Arrhenius plot, in Figure 8. The Arrhenius plot for each ambient atmosphere shows a sharp bend at about 583 K. At temperatures above this critical point, it is observed that ambients have little effect on benzene

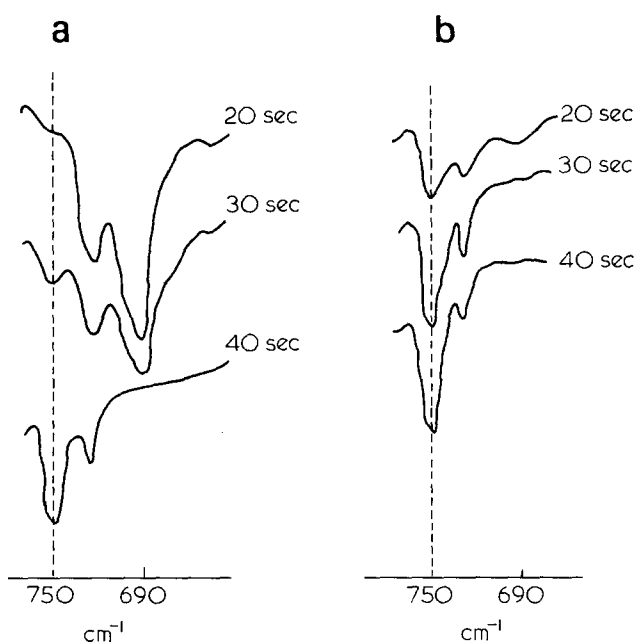


Figure 6 Infra-red spectra of PVC thermally degraded at 753 K (a) in air and (b) helium

evolution. In the temperature region below the critical point, however, the rate of benzene evolution is found to be larger in an oxidative atmosphere than in an inert one.

In order to clarify the details of the reaction, the free energy, enthalpy and entropy for activation (ΔG^* , ΔH^* and ΔS^*) were estimated by using Eyring's relation²⁶,

$$k = \kappa \frac{kT}{h} e^{-\Delta G^*/RT} \quad (4)$$

and

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (5)$$

where κ denotes the transmission coefficient and is assumed to be unity; k , h and R are the Boltzmann constant, the Planck's constant and the gas constant, respectively. The value of ΔH^* for the condensed phase was obtained from the relation,

$$\Delta H^* = E_a - RT \quad (6)$$

where E_a denotes the activation energy. These thermodynamic functions for the activated state are tabulated in Table 2.

Several reports for the thermal degradation of PVC in a

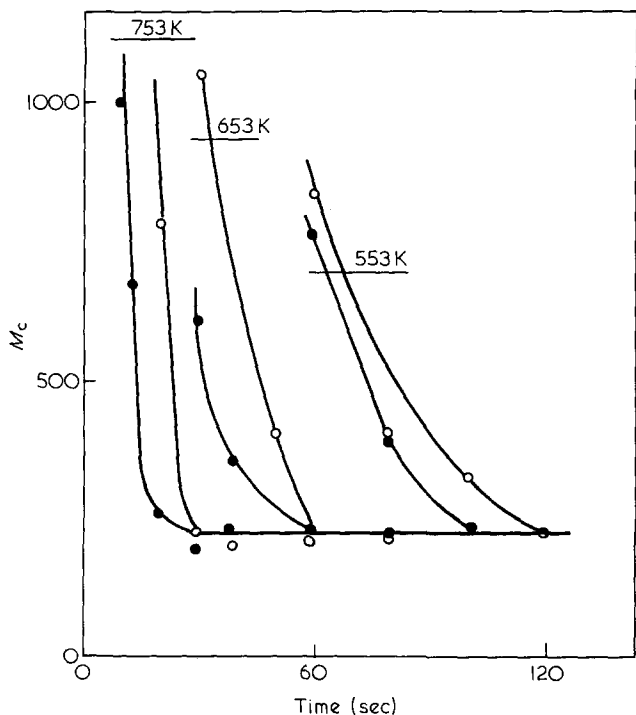


Figure 7 Relationship between M_c and heating time of PVC degraded in air and helium

Table 1 The values of t_m and t_b for M_c and benzene evolution

Temperature K	Air (sec)		Helium (sec)	
	t_m	t_b	t_m	t_b
593	107	96	90	95
654	57	52	46	45
753	31	21	20	14

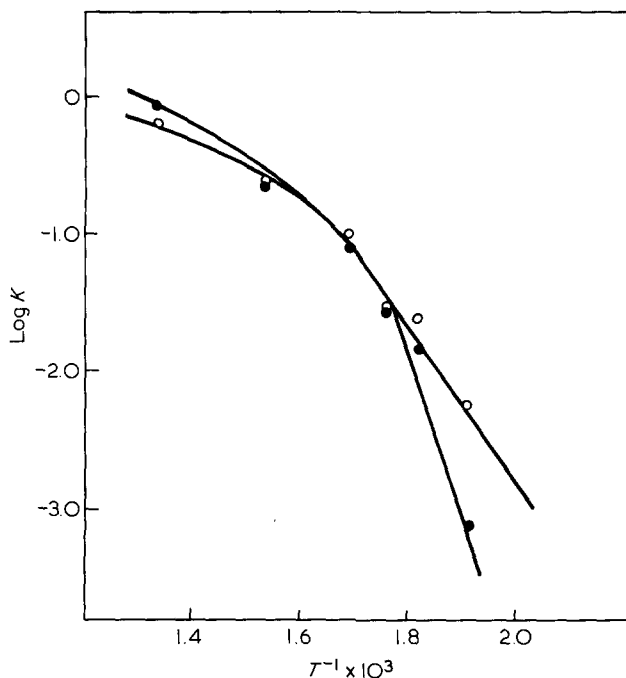


Figure 8 Arrhenius plots for benzene evolution; (O) in air and (●) helium

Table 2 Summary of benzene evolution data for PVC in air and helium

Atmosphere	Temp K	Specific rate sec ⁻¹	Activation energy kJ mol ⁻¹	Free energy kJ mol ⁻¹	Enthalpy kJ mol ⁻¹	Entropy J/K mol
Air	523	0.0057	97.1	153.1	92.9	-115.5
	548	0.0250	—	154.0	92.5	-112.1
	568	0.0311	—	158.6	92.5	-116.3
	593	0.0943	42.7	160.2	37.7	-206.7
	653	0.2140	—	172.4	37.2	-207.1
	753	0.5980	—	193.3	36.4	-208.4
Helium	523	0.0008	202.9	161.9	198.7	70.7
	548	0.0152	—	156.1	198.3	77.4
	568	0.0274	—	159.4	198.3	68.6
	593	0.0815	54.4	161.1	49.4	-188.3
	653	0.2060	—	172.8	49.0	-189.5
	753	0.8540	—	191.2	48.1	-190.0

lower temperature region have been made: (1) Stromberg *et al.*¹⁶ detected 97 mol per cent of HCl from PVC during pyrolysis at 573 K for 30 min by mass spectrometry, and indicated that the first stage of pyrolytic process was dehydrochlorination. (2) From the result of DTA measurements, Boettner *et al.*¹⁷ have shown that the endothermic peak is observed at about 573 K, and that the exothermic peaks locate in the range from near 573 K to about 873 K. (3) Chang and Solovey¹⁹ have measured quantities of HCl and benzene evolved from PVC by pyrolysis-gas chromatograph-mass spectrometric technique, and have shown that the maximum peak corresponding to HCl or benzene is found to locate at around 623 K. (4) Shimokawa *et al.*²¹ have reported that the dehydrochlorination has been completed at 603 K.

Considering these results, it can be deduced that the critical temperature observed as the inflection point of the Arrhenius plot (*Figure 8*), correlates closely with the temperature at which the rate of dehydrochlorination becomes a maximum, and that in the temperature region above this point the dehydrochlorination has been almost completed. In other words, the evolution of benzene at temperatures below the critical point is considered to be accompanied by the release of HCl.

According to Gupta and Piere²⁴, the dehydrochlorination is accelerated in the presence of oxygen, and the oxygen effect is closely related to a marked acceleration in the rate of spin generation. This fact seems to imply that the evolution of benzene at temperatures below the critical point depends on the formation of polyene sequences which are accelerated in the presence of oxygen.

As for the high temperature region, as shown in *Table 2*, ΔG^* , ΔH^* and ΔS^* are found to be little affected by atmosphere. In addition, the value of ΔH^* for the air atmosphere, about 38 kJ mol⁻¹, seems to correspond to the activation energy, estimated by Tritskii *et al.*²⁵, for C-C bond scission in polycyclic networks. From this fact, it is considered that the C-C bond scission takes place vigorously in higher temperature regions, even in non-oxidative conditions. The fact that the activation entropies in such regions are largely negative seems to imply that the form of activated complexes in both air and helium atmospheres is substantially similar to a honeycomb-like framework.

In the low temperature region, however, it is found (*Table 2*) that activation enthalpies are larger than those in the high temperature region, and that activation entropies in an oxidative atmosphere are less negative than those in the high temperature region. Particularly, in a non-oxidative condition, activation entropies exhibit positive values, i.e., both enthalpy and entropy of the activated state in a lower temperature region are larger than those in a higher temperature region. In terms of HCl evolution, it is considered that, in the low temperature region, the dehydrochlorination proceeds competitively with the cyclization even in an oxidative atmosphere. The dehydrochlorination in a non-oxidative atmosphere might be the rate determining step for the evolution of benzene in the thermal degradation of PVC.

On the basis of these observations, the following conclusions can be drawn. During pyrolysis of PVC, the

benzene derivatives are accumulated in the residues, and finally the polycyclic networks are formed. The formation of benzene derivatives and interchain linkages are closely correlated, and the evolution of benzene continues until M_c attain the limiting value of around 230.

The critical temperature for benzene evolution is found to be about 583 K. In the region above this critical temperature, benzene formation seems to be little affected by the ambient atmosphere. At temperatures below the critical point, however, the specific rate of reaction in a non-oxidative atmosphere is found to be smaller than in an oxidative one, and dehydrochlorination plays an important role in the evolution of benzene in the helium gas.

ACKNOWLEDGEMENT

The authors wish to express their gratitude to Prof H. Yamamura of Kinki University for his deep interest, and also to Dr K. Yoshizaki, President of Toyo Kohan Co. Ltd., for his support and encouragement in this work.

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