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Adsorption and Decomposition of Formic Acid Adsorbed on Pyrolyzed Polyacrylonitrile

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Infrared spectra of various pyrolyzed polyacrylonitrile and of deuterated formic acids (HCOOD, DCOOH, and DCOOD) adsorbed on it were investigated. The effect of pyrolysis temperature upon the decomposition products of formic acid adsorbed on the polymer was studied. It was found that parallelism exists between the concentration of the conjugated nitrile group and the percentage of the decomposition of formic acid adsorbed, leading to the conclusion that the active sites for the decomposition reaction are associated with the conjugated nitrile group in the case of polyacrylonitrile pyrolyzed below 300°C. On the other hand, there was a close correlation between the activity for decomposition and the number of free spins in the polymer pyrolyzed above 350°C.

Since various polymers are used as organic semiconductors, their catalytic activities have been investigated by a number of workers. Manassen and his co-workers[1,2] studied the dehydrogenation reactions catalyzed by pyrolyzed polyacrylonitrile and other polymers with defined structures, and concluded that the quinoid rings in the polymer structure are essential for the dehydrogenation reaction.

However, no detailed study has been carried out on the interaction of the reactants with the polymer under the reaction condition. Information on such interaction seems to be necessary in order to clarify the mechanism of the catalytic reactions on the poly-

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[1] J. Manassen and J. Wallach, *J. Amer. Chem. Soc.*, **87**, 2671 (1965).

[2] J. Manassen and Sh. Khalif, *ibid.*, **88**, 1943(1966).

mer. In the present work, therefore, infrared spectra of formic acid adsorbed on pyrolyzed polyacrylonitrile and also the spectral changes during the decomposition of formic acid have been investigated. From the results, the catalytic activity of pyrolyzed polyacrylonitrile has been discussed.

Experimental

Materials. Freshly distilled acrylonitrile was dissolved in water and stirred vigorously at 65°C under nitrogen while azobisisobutyronitrile was added. The white polymer thus formed was dissolved in dimethylformamide. By flowing the solution and vaporizing the solvent, a thin film was obtained. The film was cut down to 15×20 mm (about 20 mg), placed in a flame of Pyrex glass and pyrolyzed at 100–400°C in an infrared cell under evacuation. For the catalysts used in the study of the adsorption and decomposition of formic acid, the white polymer was pyrolyzed under evacuation for 3 hr at 150–500°C, the resulting polymer being powdered in a mortar.

Formic acid (Nihon Shiyaku Co. G. R.) was dehydrated by crystallization and vacuum-distilled in the presence of anhydrous copper sulfate. DCOOD (Merck) was used without further purification. DCOOH and HCOOD were prepared by the exchange of DCOOD with H_2O, and of HCOOH with D_2O, respectively.

Apparatus and Procedure. For studies of adsorption and decomposition a conventional constant volume apparatus was used. After the adsorption of formic acid vapor at room temperature, the trap attached to the reaction vessel was immersed in a dry ice-acetone mixture. Decomposition of formic acid adsorbed on the polymer was investigated by measuring the pressure increase due to decomposition. The decomposition products were hydrogen, carbon dioxide and carbon monoxide, being uncondensable at −78°C. After the experiment at room temperature, the temperature of the catalyst was raised in steps, and similar experiments were carried out. Activation energies of decomposition were determined[3,4] by comparison of the rates of decomposition at different temperatures corresponding to the same amount adsorbed. The amount of formic acid desorbed during the decomposition reaction was determined by the pressure increase which took place when the cold trap was warmed to room temperature after the reaction. Analysis of the decomposition products was carried out by gas chromatography using a 2 m silica gel column at 65°C. The isotopic abundance of H_2, HD, and D_2 was determined by a Hitachi RMU-5 mass spectrometer.

The cell used for the infrared spectroscopy of adsorption layer is similar to that used by Peri[5]. All spectra were recorded on a Hitachi EPI-S2 spectrophotometer with a NaCl prism.

Pyrolyzed polyacrylonitrile (about 10 mg) was placed in a quartz tube, evacuated at 100°C, sealed off, and the spectra were recorded on a Nihon Denshi ESR spectrometer 3BX.

Results and Discussion

Pyrolysis of Polyacrylonitrile. Figure 1 shows the infrared spectra of polyacrylonitrile pyrolyzed at various temperatures. On pyrolysis at 150°C in the region above 1800 cm^{-1}, two sharp bands appeared at about 3000 and 2235 cm^{-1}. With the rise of pyrolysis temperature the band at 3000 cm^{-1} bacame broad and increased in intensity, while the band at 2235 cm^{-1} decreased in intensity. Simultaneously, a sharp band at 2195 cm^{-1} appeared at 200°C, but disappeared completely on raising the temperature up to 350°C. Above the pyrolysis temperature 250°C, the spectrum was opaque in the region below 1600 cm^{-1}. The change in the intensities of the bands at 2235 and 2195 cm^{-1} with pyrolysis temperature is shown in Fig. 2.

As regards the pyrolysis of polyacrylonitrile a number of investigations have been carried out. According to Grassie and Hay,[6] Burlant and Parsons,[7]

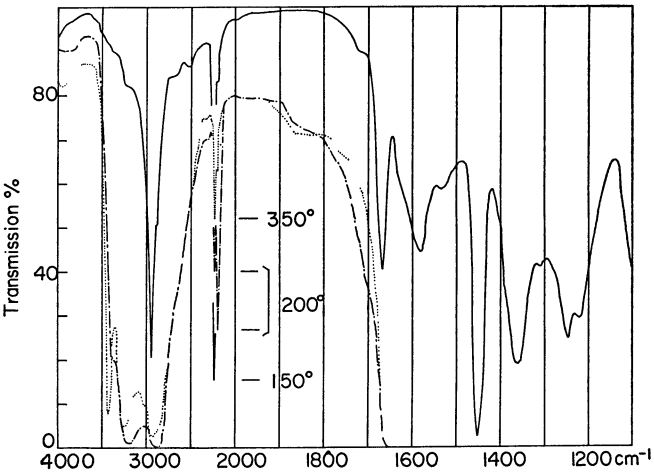

Fig. 1. Infrared spectra of polyacrylonitrile pyrolyzed at 150 (——), 200 (—·—·—), and 350°C (······).

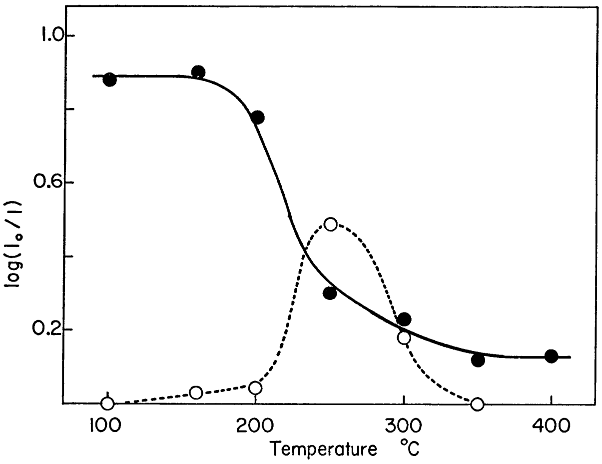

Fig. 2. Change in the band intensities at 2235 (—●—●—) and 2195 cm^{-1} (--○--○--) with pyrolysis temperature.

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3) Y. Kubokawa and H. Miyata, "Proceedings of the Third International Congress on Catalysis", Vol. 2, ed. by W. M. H. Sachtler, G. C. A. Schuit, and P. Zwietering, North-Holland Publishing, Amsterdam (1965) p. 871.

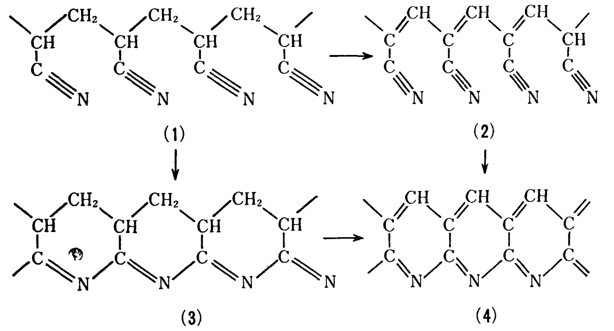
4) Y. Kubokawa and H. Miyata, *J. Phys. Chem.*, **72**, 356 (1968).

5) J. B. Peri, *Discuss. Faraday Soc.*, **41**, 121(1966).

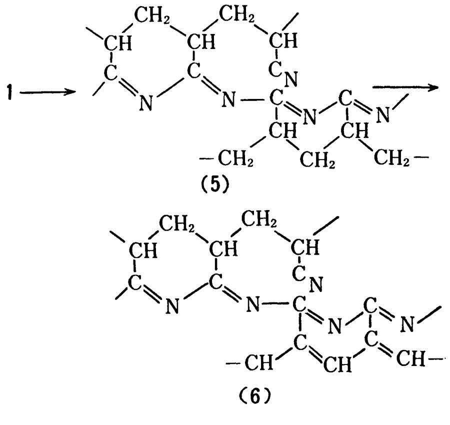
6) N. Grassie and J. N. Hay, *J. Polym. Sci.*, **56**, 189 (1962).

7) W. J. Burlant and J. L. Parsons, *ibid.*, **22**, 249 (1956).

and Conley and Bieron,[8] the pyrolysis proceeds as follows.



Aromatization of polyacrylonitrile occurs through two parallel processes; **1**→**2**→**4** and **1**→**3**→**4**. Burlant and Parsons[7] have assigned the bands at 2235 and 2195 cm^{-1} to the alkyl nitrile and to the conjugated nitrile groups, respectively. It follows that the variation in the intensities of both bands with pyrolysis temperature corresponds to the change in the concentration of both nitrile groups. In other words, on pyrolysis of polyacrylonitrile the conjugated nitrile group appears at 200°C. Its concentration passes through a maximum at 250°C and then decreases to almost zero above 350°C. On the other hand, the concentration of the alkyl nitrile group decreases monotonously with increasing pyrolysis temperature. It is seen in Fig. 2 that even above 400°C a small amount of the alkyl nitrile group still remains. Such behavior might be explained by taking into acount the occurrence of the following crosslinking reaction.[6]



Infrared Study of Interaction of Formic Acid with Pyrolyzed Polyacrylonitrile. It was found that formic acid was not adsorbed on polyacrylonitrile pyrolyzed below 150°C, where there was no band at 2195 cm^{-1} attributable to the conjugated nitrile group. After the adsorption of formic acid the transmission of the polymer decreased in the range from 3400 to 1000 cm^{-1} and the band at 2195 cm^{-1} decreased in intensity.

In order to characterize the interaction of formic acid with pyrolyzed polyacrylonitrile completely, deuterated formic acids were used in infrared measurements. The results obtained with DCOOH are shown

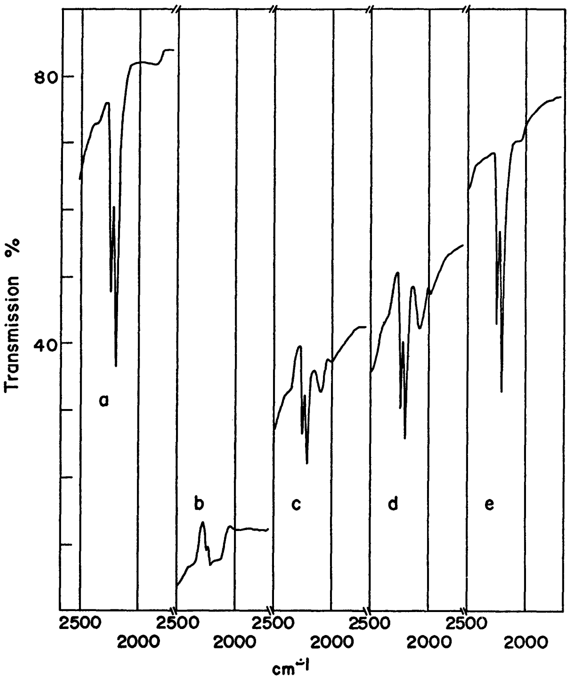


Fig. 3. Infrared spectra of DCOOH adsorbed on polyacrylonitrle pyrolyzed at 240°C.
(a) before adsorption; (b) after adsorption of 6 mmHg DCOOH at 25°C for 2 hr, and removing gas phase; (c) after evacuation at 120°C for 40 min; (d) at 120°C for 2 hr; (e) at 180°C for 1 hr.

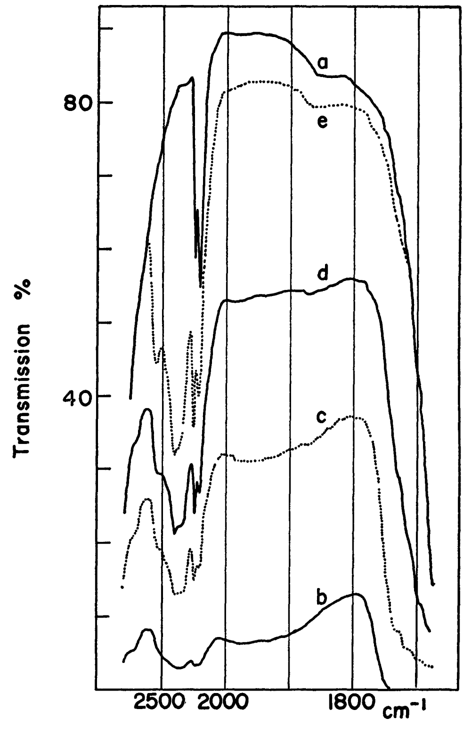


Fig. 4. Infrared spectra of HCOOD adsorbed on polyacrylonitrile pyrolyzed at 240°C.
(a) before adsorption; (b) after adsorption of 9 mmHg HCOOD at 25°C for 2 hr, and removal of gas phase; (c) after evacuation at 120°C for 30 min; (d) at 120°C for 2 hr; (e) at 180°C for 1 hr.

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[8] R. T. Conley and J. F. Bieron, *J. Appl. Polym. Sci.*, **7**, 1757 (1963)

in Fig. 3. We see that a weak band appears at 2100 cm^{-1}. On raising the temperature of the polymer to 120°C, this band shifted to 2070 cm^{-1}, and increased in intensity. It still remained after evacuation for 3 hr at 120°C, and finally disappeared by evacuation at 200°C.

Figure 4 shows the results obtained with the adsorption of HCOOD. The band at 2070 cm^{-1} was not observed. Raising the temperature up to 120°C resulted in a new band at 2380 cm^{-1} having a small shoulder at 2320 cm^{-1} not removed by evacuation at 120°C for 2.5 hr. Even after evacuation at 180°C it still remained, in contrast to the band at 2070 cm^{-1}.

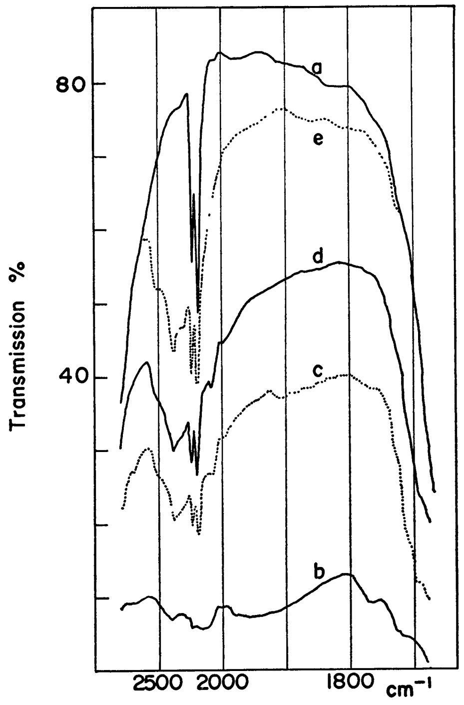

Fig. 5. Infrared spectra of DCOOD adsorbed on polyacrylonitrile pyrolyzed at 240°C.
(a) before adsorption; (b) after adsorption of 6 mmHg DCOOD at 25°C for 2 hr, and removal of gas phase; (c) after evacuation at 120°C for 30 min; (d) at 120°C for 2 hr; (e) at 180°C for 1 hr.

When DCOOD was observed, both bands at 2380 and 2070 cm^{-1} were observed as in Fig. 5. Neither band was removed by evacuation at 120°C, but at 180°C only the band at 2070 cm^{-1} was removed. Such behavior would be expected from the results obtained with DCOOH and HCOOD. Since the bands at 2070 and 2380 cm^{-1} are not observed with undeuterated formic acid, they arise from the interaction of CD and OD groups with the polymer. Considering the fact that pyrolyzed polyacrylonitrile is an efficient hydrogen acceptor as pointed out by Manassen,[1] it is concluded that such an interaction of CD and OD groups involves the D atom transfer to the polymer. Since the frequency of 2070 cm^{-1} belongs to the range of the C–D absorption, it appears that the band at 2070 cm^{-1} originates from the D atom transfer to the C atom in the polymer. Thus, another band at 2380 cm^{-1} can be assigned to the N–D vibration, which was formed by the D atom transfer to the N atom in the polymer.

Decomposition of Formic Acid adsorbed on Polyacrylonitrile pyrolyzed. The temperature of the polymer which had adsorbed a definite amount of formic acid was raised up in steps, at each of which the decomposition of formic acid adsorbed was investigated in the manner described above. Table 1 shows the amounts of formic acid desorbed and those of the decomposition products at various reaction temperatures. It is seen that at lower temperatures the decomposition products consist of carbon dioxide, hydrogen and carbon monoxide, the proportion of carbon dioxide being very large. With the rise of reaction temperature the proportion of hydrogen increases. Such a behavior suggests that at lower temperatures dehydrogenation reaction occurs predominantly, and the hydrogen formed is retained by the polymer. A similar behavior was observed by Manassen in the dehydrogenation of isopropyl alcohol.[1]

The results were obtained with polyacrylonitrile pyrolyzed at 250 and 500°C. The effect of pyrolysis temperature upon the activity of the polymer is shown in Fig. 6. It is seen that decomposition is observed

Table 1. Decomposition of formic acid adsorbed on polyacrylonitrile pyrolyzed at 250 and 500°C

Reaction temp. °C	Amount of HCOOH desorbed ccSTP/g	Activation energy kcal/mol	Total amount of the products ccSTP/g	Distribution of the products (%)		
				CO_2	CO	H_2
(a) pyrolyzed at 250°C						
70	11.5	21.5	1.46	90	1.4	8.6
120	14.7	24.6	5.76	86	2.6	11.4
180	0.58	23.7	4.63	68	2.0	30.0
240	0.00		0.57	70	13.6	17.4
(b) pyrolyzed at 500°C						
70	19.9		1.07	94	6	0
120	3.83		5.35	94	6	0
170	0.17		4.37	81	8	11
260	1.63		4.76	58	13	29
350	0.00		0.98	6	30	64

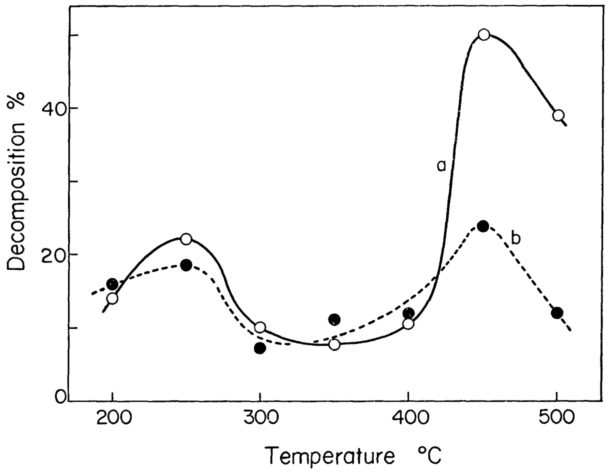

Fig. 6. Effect of pyrolysis temperature upon the activity of the polymer.
(a) 1st experiment (—○—○—), (b) 2nd experiment (--●--●--).

with only polyacrylonitrile pyrolyzed above 200°C. With increasing pyrolysis temperature, the decomposition percent of formic acid increases, showing two maxima at 250 and 450°C. The hydrogen formed during decomposition is retained by the polymer. Its effect upon the activity of the polymer was investigated by repeating the decomposition of formic acid on the same polymer. The results are shown in Fig. 6. The activity is affected slightly or not at all by the retention of hydrogen except for the measurements on the polymer pyrolyzed at higher temperatures.

The results were obtained under conditions where a definite amount (about 40 cc STP/g) of formic acid was introduced and almost all of it was adsorbed on the polymer. Table 2 shows the results for the case where the amount of formic acid introduced was so large that an appreciable amount of formic acid remained in the gas phase (formic acid pressure *ca.* 17 mmHg). It is seen that distributions of the products are almost the same in both cases, although at a reaction temperature above 350°C, the extent to which formation of carbon monoxide occurs is higher in the case when the amount of formic acid adsorbed was 151 cc.

TABLE 2. DECOMPOSITION ON FORMIC ACID ADSORBED IN THE CASE OF THE INITIAL AMOUNT OF FORMIC ACID ADSORBED 151.0 ccSTP/g[a)]

Reaction temp. °C	Amount of HCOOH desorbed ccSTP/g	Total amount of the products ccSTP/g	Distribution of the products (%) CO_2	CO	H_2
72	87.9	4.9	95	5	0
130	4.0	14.9	94	6	0
172	5.2	19.1	78	22	0
245	0.1	5.6	42	47	11
340	9.4	6.0	14	58	28

a) Polyacrylonitrile pyrolyzed at 350°C was used.

Hydrogenation and Dehydrogenation of Polyacrylonitrile During the Decomposition of Formic Acid. A comparison of the results in Figs. 2 and 6 shows that there is a parallelism between the concentration of the conjugated nitrile group and the percentage of the decomposition of formic acid adsorbed. Considering that adsorption and decomposition of formic acid take place only on the polyacrylonitrile with the conjugated nitrile group, it is concluded that the active sites for the decomposition of formic acid are associated with the conjugated nitrile group in the case of polyacrylonitrile pyrolyzed below 350°C.

It is concluded that the adsorption of formic acid involves an interaction between the hydroxyl group of formic acid and the conjugated nitrile group in the polymer, leading to the formation of the N–H bond in the temperature range above 120°C.

In addition to the N–H bond formation, the C–H bond formation occurs during the decomposition of formic acid. At present details of the C–H bond formation are not clear. As seen in Table 1, the hydrogen content in the decomposition products increases with increasing reaction temperature, suggesting that the desorption of hydrogen from the polymer takes place. In other words, the polymer hydrogenated during the decomposition of formic acid is dehydrogenated in the higher temperature range. In order to obtain information on the mechanism of dehydrogenation, the decomposition of deuterated formic acid was investigated. On polyacrylonitrile pyrolyzed at 250°C, the isotopic distribution of hydrogen is shown in Table 3. It is seen that considerable quantities of H_2 are produced in the case of DCOOD decomposition. This suggests that some portion of hydrogen desorbed does not originate from formic acid. However, taking into account the fact that the most abundant species is H_2 in the case of HCOOD, while HD in the cases of DCOOH and DCOOD, it may be concluded that a substantial fraction of hydrogen desorbed results from the combination of two hydrogen atoms, one from the CH group of formic acid and the other from the polymer.

TABLE 3. ISOTOPIC DISTRIBUTION OF HYDROGEN

Reaction temp. °C		Distribution of isotopic hydrogen (%) HCOOD	DCOOD	DCOOH
180	H_2	84	32	9
	HD	16	59	84
	D_2	0	9	7
240	H_2	87	10	19
	HD	13	78	75
	D_2	0	12	6

The activity of the polymer for the decomposition of formic acid should decrease after the reaction, since the nitrile group in the polymer is converted into the NH group after the decomposition reaction. As shown in Fig. 6, however, such a decrease in activity is hardly observed. Such behavior may be explained by assuming that the number of nitrile groups consumed by the reaction is very small compared to the total

TABLE 4. INITIAL RATE OF DECOMPOSITION OF FORMIC ACID

Deuterated formic acid	Initial rate at 120°C (CO_2 formation) mm Hg/min	Ratio
HCOOD	0.482	4.1
DCOOH	0.326	2.8
DCOOD	0.117	1.0

number of nitrile groups available for the reaction. In fact, the amount of formic acid adsorbed on the polymer, 40 ccSTP/g, is very large compared to the amount adsorbed expected from the surface area, (6.1 m^2/g), suggesting that the total number of nitrile groups is accessible to the molecule of formic acid. For example, if all the nitrile groups are available for the reaction, then only 5% of them is consumed by performing the decomposition reaction. Little or no decrease in the activity seems to be explicable.

It seems clear that during the decomposition of formic acid cleavage of the O–H bond as well as of the C–H bond occurs, although details of the latter process remain unknown. In order to obtain information on the rate-determining step for the decomposition reaction, the kinetic isotopic effect of deuterated formic acid was investigated with polyacrylonitrile pyrolyzed at 250°C. As seen in Table 4, the reaction rates decrease in the order HCOOD>DCOOH>DCOOD. It appears, therefore, that cleavage of neither the C–D bond nor the O–D bond is the rate-determining factor in the decomposition reaction.

Relation between the Number of Free Spins of Pyrolyzed Polyacrylonitrile and its Catalytic Activity. As seen in Fig. 6, the polymer pyrolyzed above 350°C exhibits a remarkable activity for the decomposition reaction. Since there are few or no conjugated nitrile groups in such a polymer, its activity is not attributable to the presence of conjugated nitrile groups. It is well-known that the polymer pyrolyzed above 350°C has the quinoid structure,[8,9] which shows the activity for hydrogen acceptor as pointed out by Manassen.[1] It appears, therefore, that the activity for the decomposition reaction arises from the presence of the quinoid structure.

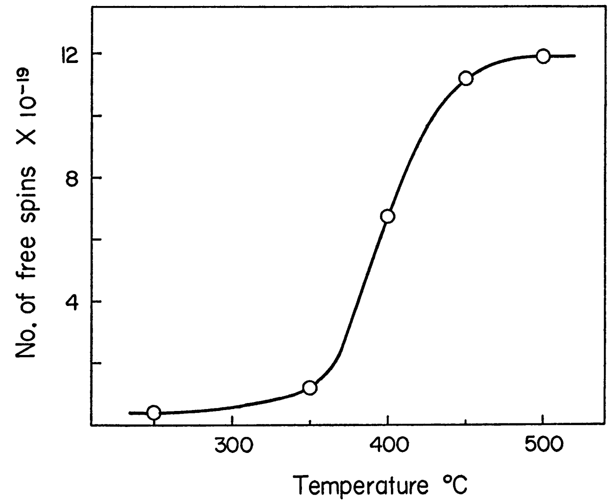

Fig. 7. Number of free spins of polyacrylonitrile pyrolyzed at various temperatures.

The number of free spins of polymer pyrolyzed at various temperatures was measured by ESR. The results are shown in Fig. 7. It is seen that the number increased markedly at temperatures above 350°C, reaching a saturated value around 450°C. A comparison of the results shown in Figs. 6 and 7 suggests that there is a close correlation between the activity for the decomposition and the number of free spins in the polymer. Although the true nature of such a correlation is not clear at present, a similar behavior has been found by Manassen,[1] and Gallard *et al.*[10]

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[9] M. Becher and H. F. Mark, *Angew. Chem.*, **73**, 641 (1961).

[10] J. Gallard, A. R. Pecher, and Ph. Traynard, *J. Catal.*, **13**, 261 (1969).