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Time-Courses of the Electron Spin Resonance Spectra of Radicals Generated in Binary Powders of Glycolic Acid and Silica-Alumina

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Electron spin resonance (ESR) spectra of radicals generated in binary powders of glycolic acid and silica-alumina were recorded. The spectral shape was dependent on content of glycolic acid and on the atmosphere used, but remained almost unchanged under given conditions throughout the experiments. However, spectral intensity was weak immediately after mixing, increased thereafter, eventually reached a maximal value, and finally began to decrease. The maximal amount of radicals and the duration of the maximal amount of radicals were found to be dependent on the calcination temperature of silica-alumina, on the atmosphere used, and on the temperature of storage. The rate of the contact reaction of glycolic acid on silica-alumina seemed to increase with increase in the maximal number of radicals.

Keywords ESR; radical number; time-course; binary powder; glycolic acid; silica-alumina; contact reaction rate; calcination temperature; atmosphere

An acid–base indicator adsorbed on solid-acid sites on the surface of an aluminosilicate becomes colored corresponding to the acidity and acid strength.[1] However, it usually takes 2—3 d as judged visually to reach equilibrium.[2] Therefore, the authors thought that it might be possible to observe the development or decay of the equilibrium state in binary powders containing an aluminosilicate and a general organic compound by the use of an electron spin resonance (ESR) spectrometer. We have already observed the formation of radicals in binary powders of a saccharide and a metal oxide,[3,4] and of a metal oxide and an organic compound[5] upon stirring in a glass vessel. In that case, we reported that the amount of radicals was small immediately after mixing, increased gradually thereafter, reached a maximal value, and then remained almost unchanged.

Later, the ESR spectra of radicals generated in binary powders of glycolic acid (GA) and silica-alumina (SA) were followed for a period of up to 5 years after mixing. We found that the number of radicals began to decrease from its maximal value after a long period. In this paper, we describe the results in detail, taking into account the contact reaction of GA on the surface of SA.

Results and Discussion

Time-Courses of ESR Spectra Figure 1 shows typical ESR spectra of radicals generated in binary powders of SA calcined for 5 h at 600 °C (SA calcined for 5 h at 200, 400, or 600 °C are abbreviated henceforth as SA_{200}, SA_{400}, or SA_{600}, respectively) and GA in an atmosphere of nitrogen (Fig. 1-a and 1-b), dried air (Fig. 1-c), or humid air (RH = 60%, Fig. 1-d). It can be seen from Fig. 1 that the shape of the ESR spectrum is dependent on the content of GA and on the atmosphere used. The spectral shape of radicals generated in a binary powder of GA (0.1 wt%) and SA_{600} in an atmosphere of dried air or humid air (RH = 60%) was almost the same as that of radicals in an atmosphere of nitrogen (shown in Fig. 1-a). An increase in the content of GA (0.1 wt% → 10 wt%) results in a change in the spectral shape from that shown in Fig. 1-a to that shown in Fig. 1-b in an atmosphere of nitrogen, from that shown in Fig. 1-a to that shown in Fig. 1-c in an atmosphere of dried air, or from that shown in Fig. 1-a to that shown in Fig. 1-d in an atmosphere of humid air (RH = 60%). As far as the time-courses of spectral shapes were concerned, the spectral shape did not change from immediately after the mixing in an atmosphere of nitrogen or of dried air. When humid air (RH = 60%) was used as an atmosphere, however, the spectral shape changed slightly during the first 120 h after mixing, and then became constant. Very little change in spectral shape was observed upon alteration in the calcination temperature (200—600 °C) of SA.

Characterization of Radicals Except for the region of 3250—3320 G, a similar ESR spectrum to that illustrated in Fig. 1 was obtained when SA was mixed with ascorbic acid, glycerol, indole, or salicylic acid, or when SA powder was irradiated with a mercury lamp (500 W). The spectral shape was quite different when GA was mixed with a silica-gel, an alumina, or a mordenite. Therefore, the ESR signals shown in Fig. 1 might be attributed mainly to electrons or holes trapped by a macromolecule (SA) and presumably affected by adsorbed GA.

The spectrum due to organic radicals, appearing within

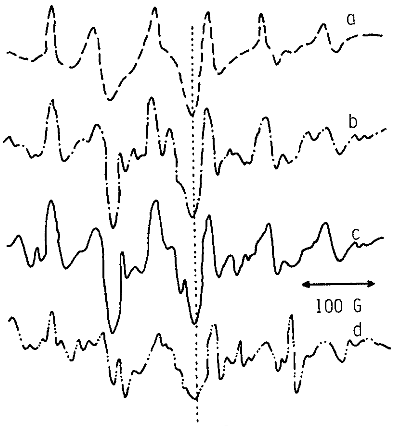

Fig. 1. ESR Spectra of Radicals Generated in Binary Powders of Glycolic Acid and Silica-Alumina in an Atmosphere of Nitrogen, of Dried Air, or of Humid Air

a: content of glycolic acid, 0.1 wt%; atmosphere, nitrogen. b: content of glycolic acid, 10 wt%; atmosphere, nitrogen. c: content of glycolic acid, 10 wt%; atmosphere, dried air. d: content of glycolic acid, 10 wt%; atmosphere, humid air (RH = 60%). Silica-alumina was calcined for 5 h at 600 °C prior to use. The mixed powder was left in the respective atmosphere at 25 °C for at least 170 h after mixing. Then an ESR spectrum was recorded at room temperature with the instrumental settings described in the experimental section. A signal having $g = 2$ was observed at 3285 G with our machine.

the region of 3250—3320 G, was estimated from the signals of a GA–SA mixture obtained at a decreased power (1 mW) and a decreased modulation amplitude (1 G) by subtracting those of ultraviolet (UV)-irradiated SA. This spectrum was 60 G wide and was composed of two peaks. It was similar to the spectrum of a diglycolic acid (DGA) and SA mixture stored at 80 °C minus that of UV-irradiated SA. Moreover, Kurita[6] reported an analysis of the hyperfine structure of DGA radicals in an irradiated single crystal, which was composed of six spectral bands (two of them were observed in this study). Therefore, the signals due to organic radicals in this region may be attributed to DGA radicals. Next, the number of DGA radicals was found to vary synchronously with that of radicals in SA. At a high power (20 mW) and a high modulation amplitude (6.3 G), the number of DGA radicals was estimated to be at most 6% of the total number of radicals.

Time-Courses of the Numbers of Radicals The intensity of the ESR spectrum varied remarkably with time. Figure 2 shows the effects of calcination temperature of SA, of the atmosphere, and of the temperature of storage of the mixed powder on the time-course of the number of radicals generated in a binary powder of GA (10 wt%) and SA (150—200 mesh). As shown in Fig. 2 the amount of radicals generated in a binary powder of GA and SA_{200} stored at 25 °C in an atmosphere of dried air is small immediately after mixing, increases gradually with time, reaches a maximum at 100 h after mixing, remains unchanged at the maximal value for a long period (250 d), and finally begins to decrease rather abruptly. The same tendency was observed in the time-course of the number of radicals generated in a mixed powder containing SA_{600}. However, the increase in the number of radicals to a maximal value is not shown in Fig. 2, because the maximal number of radicals was attained at 3 h after mixing even for the slowest case (stored at 25 °C in an atmosphere of humid air). Generally speaking, the maximal amount of radicals and the duration of the maximal number of radicals depend on the calcination temperature of SA, on the atmosphere used, and on the temperature of storage of the mixed powder. Increase in the calcination temperature of SA and in the temperature of storage results in an increase in the maximal number of radicals and a decrease in the duration of the maximal number of radicals. The number of radicals when stored at 25 °C in dried air is almost the same as that when stored at 25 °C in an atmosphere of nitrogen, but the duration of the maximal value for the former is considerably shorter than that for the latter. A remarkable decrease in the maximal number of radicals and its duration are observed when the powder is stored in humid air (RH = 60%). In addition, the slope of the decrease curve of the number of radicals from its maximal value in humid air is much greater than that in a dried atmosphere. This slope was found to increase with increase in the relative humidity of a moisture-containing atmosphere. The maximal number of radicals and the duration of the maximal number of radicals generated in a binary powder of GA (10 wt%) and SA_{400} were found to be intermediates between the values for SA_{600} and those for SA_{200}. In addition, these values for SA_{400} showed almost the same dependences on calcination temperature of SA, on atmosphere, or on temperature of storage as those for SA_{200} or SA_{600}. In this case, the maximal number of radicals was reached at less than 70 h after mixing.

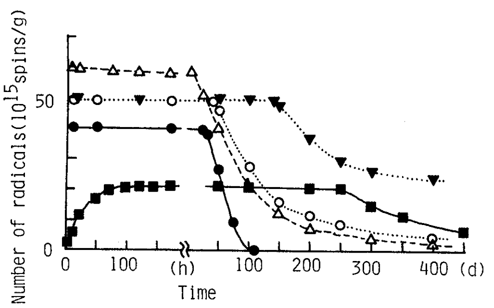

Fig. 2. Effects of Calcination Temperature, Atmosphere, and Temperature of Storage on the Time-Course of the Number of Radicals Generated in the Binary Powder of Glycolic Acid (10 wt%) and Silica-Alumina

●, silica-alumina, SA_{600}; atmosphere, humid air (RH = 60%); storage temperature of the mixed powder, 25 °C. ○, silica-alumina, SA_{600}; atmosphere, dried air; storage temperature of the mixed powder, 25 °C. △, silica-alumina, SA_{600}; atmosphere, dried air; storage temperature of the mixed powder, 80 °C. ▼: silica-alumina, SA_{600}; atmosphere, nitrogen; storage temperature of the mixed powder, 25 °C. ■: silica-alumina, SA_{200}; atmosphere, dried air; storage temperature of the mixed powder, 25 °C.

Contact Reaction of Glycolic Acid on the Silica-Alumina Surface As described above, DGA radicals were detected when GA was mixed with SA in an atmosphere of nitrogen or of dried air. Therefore, the contact reaction may begin with the formation of an unstable GA radical ($\dot{C}HOHCOOH$) from GA, followed by a rapid condensation with excess GA, forming the somewhat more stable DGA radical ($HOOCCH_2O\dot{C}HCOOH$).

GA is known to produce oxalic acid by oxidation, and glycolide by condensation.[7] In an atmosphere of oxygen, the production of oxalic acid was confirmed by comparing the infrared (IR) spectrum of the powdery product with that of an authentic sample. In this case, the ratio of oxalic acid to GA seemed to increase with time. At last, no GA molecule was observed spectroscopically when the number of radicals began to decrease from its maximal value, although the shape of the ESR spectrum was almost the same as that of a binary powder of GA and SA possessing the maximal number of radicals. In an atmosphere of nitrogen or of dried air, the CH stretching vibration of GA (around 2950 cm^{-1}), for example, became unobservable concomitantly with the start of a decrease in the number of radicals from a maximum.[8] Since the amount of radicals in a binary powder of SA and oxalic acid was small ($< 1 \times 10^{14}$ spins/g), the start of the decrease in intensity of the ESR spectrum from a maximal value may suggest almost complete disappearance of GA in contact with SA.

GA is hydrolyzed under humid conditions.[7] Though the reaction product was not characterized, GA became undetectable by IR spectroscopy when the number of radicals began to decrease.

In any event, the maximal number of radicals and the duration of the maximal number of radicals seem to be useful measures of the rate of contact reaction on the surface of SA.

Experimental

Materials Commercial GR grade GA was used after being recrystallized from water and dried under a vacuum. Nikki Kagaku N631-L Type SA was calcined for 5 h at 200, 400, or 600 °C.

ESR Measurement ESR spectra of mixed powders were obtained with a JES-FE3X type spectrometer[9)] (X band, 100 kHz modulation) with the following instrumental settings[10)]: power, 20 mW; modulation amplitude, 6.3 G; scan rate, 31.25 G/min; time constant, 1 s; gain, 2 × 1000. Since SA and GA powder provided no ESR signal, the number of radicals was estimated by integrating twice the first derivative curves ranging from 2900 to 3600 G.

Procedure GA (0.1—10 wt %)[11)] was mixed with SA (150—200 mesh) in an atmosphere of nitrogen, of dried air, or of humid air and was shaken vigorously in a glass vessel for 15 min. This powder was stored in a desiccator, a glass vessel, or an ESR cell in an atmosphere of nitrogen, of dried air, or of humid air at 25—80 °C in the dark. Powders thus prepared were shaken at 10—12 h intervals. Dried air or humid air was obtained using a desiccator by the usual method.[12)] The temperature of storage of a mixed powder was adjusted by the use of a thermostat.

References and Notes

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8) The relationship between the end point of the contact reaction and the start of the decrease in the number of radicals from the maximum was not quantitatively exact, probably because powders were not allowed to be shaken for many years after mixing, except for 3 min at 10—12 h intervals. However, the absence of the CH stretching vibration of GA (around 2950 cm^{-1}) was noted concomitantly with the start of the decrease in the number of radicals from its maximal value in binary powder of GA (10 wt%) and SA$_{600}$ entirely without stirring.
9) H. Kashiwagi and S. Enomoto, *Chem. Pharm. Bull.*, **30**, 17 (1982).
10) The microwave power and the modulation amplitude employed here may be too great for usual measurement of an ESR spectrum of organic radicals. However, the spectral intensity from organic radicals was sufficiently small and was found to vary simultaneously with that from radicals in SA. In addition, the latter was not saturated even at such a high power and was found to be strong enough to permit the quantitative determination of the number of radicals in the binary powder. Needless to say, the saturation of organic radicals observed in the region of 3250—3320 G leads to considerable error (at most 6%) in the quantitative determination of the number of radicals. No further splitting was observed in the ESR spectrum of a GA–SA mixture at a decreased modulation amplitude.
11) A large content of GA (0.1—10 wt%) was employed in the light of mechanochemical considerations of contact reactions. However, it frequently causes broadening of the ESR spectrum and prevents the analysis of hyperfine structures.
12) H. Yokoi, S. Enomoto, and S. Takahashi, *Yakugaku Zasshi*, **98**, 418 (1978).