The Review of Physical Chemistry of Japan Vol. 28 (1958)

STABILITY FOR OXIDATION OF UNSATURATED FATTY ACIDS IN THEIR UREA ADDUCT CRYSTALS

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Several investigators[1] have made the detailed examinations of the phenomenon that urea formed the crystalline adducts with long straight-chain organic compounds, and have established new techniques for the separation of organic substances. A. E. Smith[2] determined the crystal structure of urea adducts of *n*-hydrocarbons by X-ray analysis, and showed that the unit cell was hexagonal ($a=8.23$ Å, $c=11.00$ Å), and the urea molecules formed a hollow channel structure by hydrogen bonds, in which the long hydrocarbon molecules were enclosed in parallel with the c axis. It seemed, therefore, that the crystalline urea adducts of unsaturated fatty acids should be different from the free acids with respect to oxidation. H. Schlenk and R. T. Holman[3] compared the oxygen uptakes of pure linoleic and linolenic acids with those of their urea adducts at 37°C, and found that the acids in urea adducts did not absorb oxygen for a month, whereas the free acids were oxidized rapidly. It was seen that the restricted space within the crystal lattice was too narrow to permit the free penetration of oxygen or the formation of peroxide. Furthermore, as the oxidation of unsaturated fatty acids was known to be a chain reaction, it seemed to be difficult for such a mechanism to take place between the separated molecules in urea adducts.

In the present experiments, the oxidation of unsaturated fatty acids and their urea adducts is examined under several conditions by air and ozone. Some knowledge for the stability of urea adduct crystals is obtained with respect to oxidation.

Experimentals

The unsaturated fatty acids used in this investigation are refined repeatedly by means of the fractional crystallization in urea adduct forms and the vacuum distillation. They have the physical and chemical properties as shown in Table 1.

The crystalline urea adducts of the fatty acids used are prepared from methanol solutions and recrystallized from isopropyl alcohol. The compositions of the acids in urea adducts are as follows: oleic, 26.4 wt. %, linoleic, 26.0% and linolenic, 26.1%. The samples for oxidation are powdered in an agate mortar and, if necessary, milled with NaCl crystals in weight ratio of 1 : 1.

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[1] W. Schlenk, Jr., *Annalen*, **565**, 204 (1949)
O. Redlich, C. M. Gable, A. K. Dunlop, and R. W. Millar, *J. Am. Chem. Soc.*, **72**, 4153 (1950)
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D. Swern, L. P. Witnauer and H. B. Knight, *J. Am. Chem. Soc.*, **74**, 1655 (1952) *etc.*

[2] A. E. Smith, *J. Chem. Phys.*, **18**, 150 (1950)

[3] H. Schlenk and R. T. Holman, *J. Am. Chem. Soc.*, **72**, 5001 (1950)

Table 1 Properties of the sample fatty acids

Acids	Oleic	Linoleic	Linolenic
Refractive index, n_D^{20}	1.4590	1.4700	1.4798
Density, d_4^{20} (g/cc)	0.896	0.903	0.905
Iodine value	89.6	181	272
Neutralization value	199	201	201

The experiments are performed by the following methods:

i) The dry and CO_2-free air is flowed with the velocity of 100 liter/hour through the fatty acids and their urea adducts which are kept in the constant temperature bathes of 30, 50 and 80°C.

ii) The samples in a high pressure vessel are kept under the air of the pressure of 500 kg/cm^2 at room temperature (10~15°C). If necessary, the ultra-high pressure vessel[4] is used in the air of 4000 kg/cm^2.

iii) The samples are exposed to the oxygen containing 6~8% ozone at the room temperature (15~20°C).

The results of the oxidation are measured from the decreases in iodine values of Wijs method[5].

Results and Considerations

Oxidation by flowing air The decreases in iodine values of oleic, linoleic and linolenic acids and their urea adducts are shown in Fig. 1, where the full curves indicate the free acids and dotted lines their urea adducts. The values of rate constant, k, and activation energy, E, which

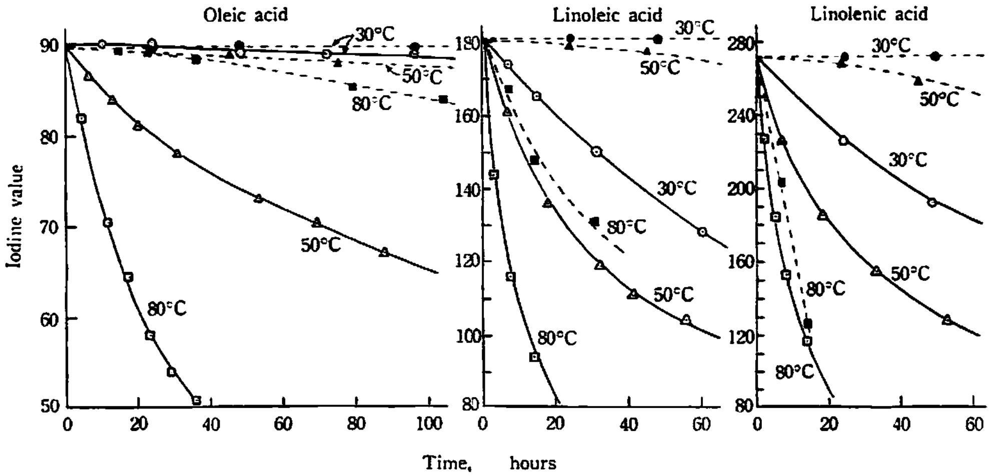

Fig. 1 Air oxidation by the flow method

The full curves indicate the free acids and the dotted curves show the acids in urea adducts.

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[4] R. Kiyama, *This Journal*, 19, 1 (1945)

[5] A. W. Ralston, *Fatty Acids and Their Derivatives*, p. 301, Wiley (1948)

Table 2 Rate constant k and activation energy E of the air oxidation by flow method

Acids		Oleic		Linoleic		Linolenic	
		Free acid	Urea adduct	Free acid	Urea adduct	Free acid	Urea adduct
k ($10^{-2}hr^{-1}$)	30°C	0.022	0	0.58	0	0.78	0
	50°	0.52	0.012	1.7	0.055	2.6	0.088
	80°	2.3	0.035	6.9	1.4	8.8	4.3
E (kcal/mole) calc. between 50° and 80°C		11	7.9	10	24	9.0	29

are calculated as the first order reaction[6] are tabulated in Table 2. The rates of oxidation of the free acids increase with increasing temperature and unsaturation. The urea adducts of the three acids are not oxidized for 600 hours at 30°C, but slowly at 50°C and considerably at 80°C. And at the same temperature, the rates become larger with the increasing unsaturation of acids. As the weight of urea which is brought off by flowing air is negligibly small even at 80°C[7], it seems that the crystal lattice of urea adduct becomes considerably unstable near this temperature. Although H. B. Knight and coworkers[8] measured the dissociation temperatures of urea adducts and found that the hexagonal urea adduct crystal of oleic acid dissociated into free acid and the microcrystals of urea at 110°C, it is likely that the oxidation of oleic acid in urea adduct form begins at lower temperature.

Oxidation by air under high pressures The oxidation of the free acids and their urea

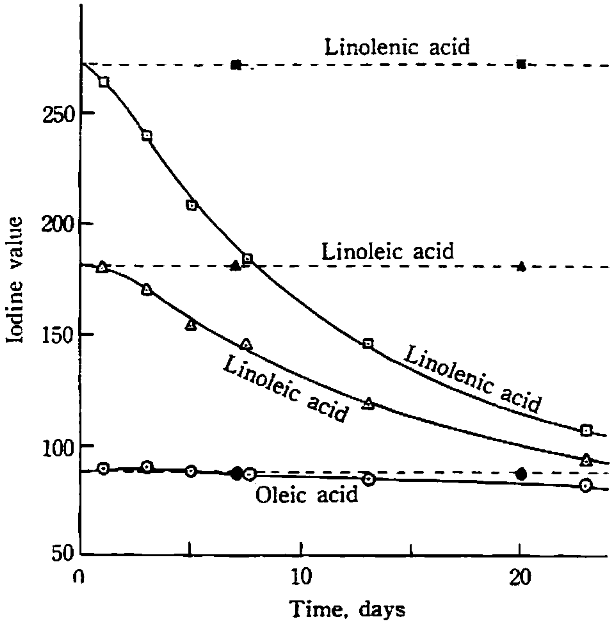

Fig. 2 Air oxidation under 500kg/cm² at 10~15°C

The free acids are shown by the full curves and the acids in urea adducts by the dotted lines.

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6) L. A. Hamilton and H. S. Oloott, *Ind. Eng. Chem.*, 29, 217 (1937)

7) K. Suzuki, S. Onishi, T. Koide and S. Seki, *Bull. Chem. Soc. Japan*, 29, 127 (1956)

8) H. B. Knight, L. P. Witnauer, J. E. Coleman, W. R. Noble, Jr., and D. Swern, *Anal. Chem.*, 24, 1331 (1952)

adducts under 500 kg/cm^2 air is shown in Fig. 2 as the decreases in iodine values with time. As the urea adducts of the three acids are not oxidized for two months, the samples are kept under 4000 kg/cm^2 air for three hours at 14°C. But no change in iodine values is found. It can be concluded that the urea lattice is stable under these hydrostatic pressures and the protection for oxidation is complete.

Ozonation The unsaturated fatty acid reacts with ozone, adding quantitatively one molecule of ozone to each double bond. In consequence of such a simple mechanism, it seems likely that ozonation may occur on the separated molecules in urea adduct crystals if there could be the spaces for the penetration of ozone and the formation of ozonide ring. At first, 6~8 wt. % ozonized oxygen is flowed by 10 liter/hour through the free acids and their urea adducts, individually, and the amount of unabsorbed ozone is measured during the reactions. In Fig. 3, the volume of unabsorbed ozone per minute is plotted against the time, in the cases of oleic acid and its urea adduct. It is found that the free acids are ozonized rapidly and quantitatively, and that the urea adducts do not absorb ozone at all. Furthermore, the urea adducts of the three acids are kept in the atmosphere of 6~8% ozonized oxygen at room temperature, and no ozonide can be detected after 36 days. These results show that the hollow channel structure of urea protects completely the double bonds against the addition of ozone.

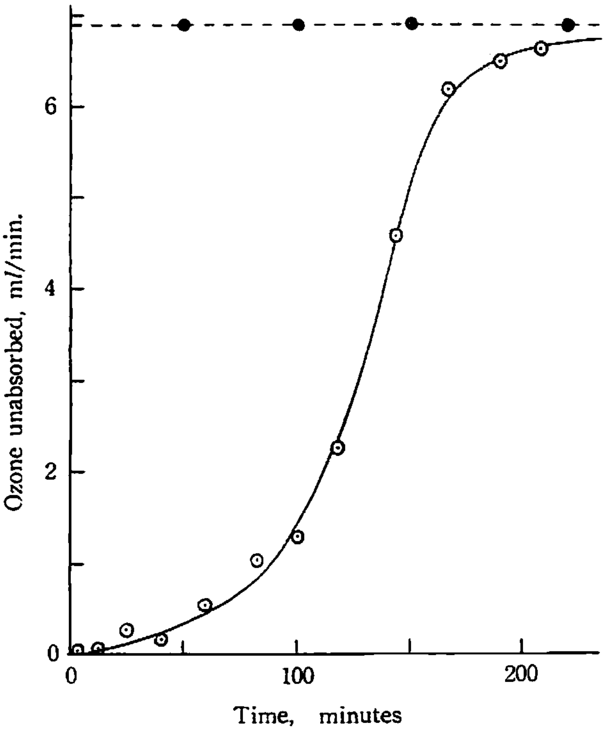

Fig. 3 Ozonation of oleic acid and its urea adduct by flow method at 15°C

The flow velocity of oxygen containing 6.05 wt. % ozone is 10 liter/hour, the free acid used is 11.350 gram, and the theoretical time of full addition of ozone is 131 minutes. The free acid is shown by the full curves and the urea adduct by the dotted line.

Oxidation of milled urea adducts The urea adducts milled with NaCl crystals are kept in the atmospheric air and 500 kg/cm^2 air at room temperature (10~15°C). After 16 days, it is found that the unsaturated fatty acids in the milled urea adducts react partly with oxygen, as

Table 3 Iodine values in air oxidation at 10~15°C

Acids			Oleic	Linoleic	Linolenic
Before reactions			89.6	181	272
After 16 days	At 1 atm	Free acid	87.9	138	183
		Milled urea adduct	88.6	162	257
	Under 500 kg/cm²	Free acid	84.5	108	135
		Milled urea adduct	86.8	158	236

shown in Table 3, where the decreases in iodine values are compared with the free acids. Furthermore, when the milled samples are kept in the atmosphere of ozonized oxygen, 4~5% of the three acids in urea adducts are found to be ozonized in 5 days, and the amount of the ozonides does not change until 15 days. This means that part of the crystal lattice is probably broken by the milling with NaCl crystals. From this point of view, the urea adduct of oleic acid milled with NaCl crystals is examined by Debye-Scherrer method of X-ray analysis. The results show the presence of the tetragonal crystals of urea. Therefore, it seems probable that, as part of the crystal lattice of urea adducts is mechanically broken, part of the free acid molecules in urea adducts is exposed in air or ozone and oxidized.

The author has greatly pleasure in expressing his sincere thanks to the late Prof. R. Kiyama, under whose direction this work was done, and to Prof. R. Goto for the valuable advice and suggestions on the treatment of fatty acids used in this research. Opportunity is taken to express gratitude to Prof. C. Araki for the use of the high-power ozonizer, to Prof. A. Tachiiri for the X-ray analysis and to Mr. N. Matsumoto for assistant in analysis, in Kyoto Technical University. The author is also indebted partly to the Department of Education for the Grant in Aid to the Researches by Junior Researchers in Research Institutions.

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