Metalloporphyrin-Catalyzed Decomposition of Ethyl Azidoformate

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Ethyl azidoformate (2) was thermolyzed in the presence of metalloporphyrins. CoTPP accelerated the decomposition rate of 2 and resulted in the preferential formation of the hydrogen-abstraction product (urethane). On the other hand, NiTPP and CuTPP had no influence on the decomposition behavior of 2.

Reaction of the metalloporphyrins with nitrene species results in modifications of the porphyrin rings such as N-acylamination or ring expansion.[1] However, use of the metalloporphyrins as the perturbant of the nitrene reaction by formation of the nitrenoid complex has been almost uninvestigated although zero-valent metals such as Cu^0 or Fe^0 are known to generate the nitrenoid complexes.[2]

We now report the finding that cobalt tetraphenylporphyrin (CoTPP, 1a) accelerates the decomposition rate
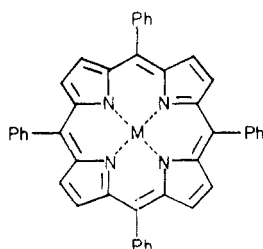
1a, M = Co(II)
b, M = Ni(II)
c, M = Cu(II)

of ethyl azidoformate (2) and causes perturbation of the reaction pathways of 2. Table I shows the decomposition rate of 2 in the presence and absence of metalloporphyrins. Volatile products derived from the reaction of 2 in the presence and absence of metalloporphyrins are listed in Table II. Runs with nickel tetraphenylporphyrin (NiTPP, 1b), copper tetraphenylporphyrin (CuTPP, 1c), and no catalyst in CCl_4 and benzene solvents are omitted in Table II because the extent of reaction was too small to permit the detection of products. From Table I and II, it is apparent that 1b and 1c have no effect on the decomposition rates of 2 and the reaction pathways of the nitrene species derived from 2.

On the other hand, the data reveal that 1a catalytically accelerates the decomposition rate of 2 and distinctly changes the reaction pathways of 2. Thus, in the presence of 1a, the hydrogen abstraction product (urethane) was produced as the only volatile product in the reaction with benzene, cyclohexene and cyclohexane and as the preferential product together with minor amounts of azepines and the C–H insertion product in the reaction with p-xylene. Though the action of 1a as the source of an electron was expected to allow the nucleophilic addition of the nitrenoid derived from the reaction of 2 with 1a to an activated olefin such as acrylonitrile, such a product could not be found. These product distributions are in sharp contrast with the reaction of the discrete nitrene

Table I. Observed First-Order Decomposition Rates of 2 in the Presence and Absence of Metalloporphyrins

metalloporphyrin	solvent	reaction temp, °C	additive	$10^4 k$, s^{-1}
1a	CCl_4	77	none	1.3
1a	CCl_4	77	CH_2=CHCN	1.4
1b	CCl_4	77	none	<0.01
1c	CCl_4	77	none	<0.01
none	CCl_4	77	none	<0.01
1a	benzene	80	none	0.12
1a	benzene	80	cyclohexene	2.4
1a	benzene	80	cyclohexane	1.8
1a	benzene	80	CH_2=CHCN	0.12
1b	benzene	80	cyclohexene	<0.05
1c	benzene	80	cyclohexene	<0.05
none	benzene	80	cyclohexene	<0.05
1a	p-xylene	138	none	8.7
1b	p-xylene	138	none	3.0
1c	p-xylene	138	none	2.6
none	p-xylene	138	none	2.8

Table II. Products Derived from Decomposition of 2 in the Presence and Absence of Metalloporphyrins[a]

| metalloporphyrin	solvent	additive	product (% yield)
1a	CCl_4	CH_2=CHCN	NH_2COOEt (21)
1a	benzene	none	NH_2COOEt (42)
1a	benzene	cyclohexene	NH_2COOEt (47)
1a	benzene	cyclohexane	NH_2COOEt (45)
1a	benzene	CH_2=CHCN	NH_2COOEt (41)
1a	p-xylene	none	NH_2COOEt (68), 3 (15), 4 (10), 5 (1)
1b	p-xylene	none	NH_2COOEt (2), 3 (52), 4 (28), 5 (4)
1c	p-xylene	none	NH_2COOEt (2), 3 (51), 4 (34), 5 (7)
none	p-xylene	none	NH_2COOEt (2), 3 (53), 4 (34), 5 (7)
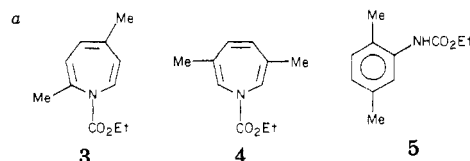
species derived from 2 becuase azepine, aziridine, and the C–H insertion product are the main products derived from the reaction of that species with aromatic hydrocarbon, cyclohexene, and cyclohexane, respectively.[3] Although the chloride abstraction product, *N,N*-dichlorourethane (6)

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Scheme I
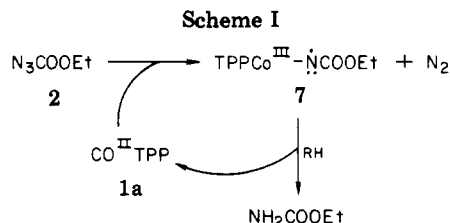
might be anticipated to be formed in the reaction of **2** in CCl$_4$ containing **1a**, **6** could not be detected. The failure of detection of **6** is probably due to the decomposition following after formation of **6** under our reaction conditions, as shown by the control experiment which revealed that authentic **6** decomposed under the same conditions.

Concerning the reaction mechanism of the thermolysis of **2** in the presence of **1a**, the possibility that **1a** might promote intersystem crossing of the singlet to triplet nitrene might be derived from a first glance at the results since the triplet nitrene species is known to preferentially give abstraction products.[4] However, this mechanism is less likely since the triplet nitrene can not only abstract hydrogen but also add to double bonds to give aziridines,[5] while the reaction of **2** with cyclohexene in the presence of **1a** gave no aziridine from cyclohexene. It seems probable from comparison of the catalyzed and noncatalyzed decomposition rates of **2** that azepines and the C–H insertion product as minor products in the CoTPP-catalyzed thermolysis reaction of **2** with *p*-xylene were derived from the free nitrene species generated noncatalytically. The behavior of the species derived from the thermolysis of **2** in the presence of **1a** resembles very much that of aminyl radicals which are reported to selectively give hydrogen abstraction products.[6] Thus, although it is not conclusive, we consider as a possible pathway the mechanism in which the aminyl radical–cobalt(III) complex **7** is generated by one-electron transfer to the azido group of **2** from **1a** and abstracts a hydrogen followed by reductive elimination of the resulting amino ligand to give urethane and regenerate **1a** (Scheme I). Table I indicates that the decomposition rate of **2** in benzene containing acrylonitrile or no additive is not so much accelerated by **1a** as that in CCl$_4$ or benzene

in the presence of cyclohexene or cyclohexane.

In our assumed mechanism, the decomposition rate of **2** depends upon a concentration of the catalyst **1a** in the steady state which is controlled by the regeneration rate of **1a** from the intermediate **7** as shown in Scheme I. Thus, it seems reasonable to us that only a little acceleration of the decomposition rate of **2** by **1a** in benzene containing acrylonitrile or no additive reflects a low concentration of the catalyst **1a** in the steady state. This may be caused by the sluggish regeneration of **1a** from the intermediate **7** due to slow hydrogen abstraction of **7** from benzene or acrylonitrile. Consistent with this assumed mechanism, cobalt is known to adopt +2 and +3 oxidation states in metalloporphyrins while nickel and copper are known to adopt only a +2 oxidation state.[7] Thus, it seems to be likely that **1a** perturbs the decomposition of **2** in a one-electron redox fashion while **1b** and **1c** have no effect on the decomposition of **2**.

Experimental Section

Materials and Equipment. Metalloporphyrins were prepared according to the method of Rothemund.[8] Ethyl azidoformate was prepared by the procedure reported by Lwowski and Mattingly.[3b] IR spectra were recorded on a Hitachi EPI-G3 spectrometer. NMR spectra were recorded on a Varian EM-360 spectrometer. VPC analyses were done on a Hitachi 063 instrument equipped with a 200 × 0.4 cm column packed with 10% PEG on Uniport.

Thermolysis Reaction of 2 in the Presence of Metalloporphyrins. To a refluxing mixture of 1 mmol of metalloporphyrin, 8 mmol of additive, and 19 mL of solvent under an atmosphere of nitrogen was added a solution of 1 mmol of **2** in 1 mL of solvent via syringe. Nitrogen evolved was collected over water and its volume was periodically measured. After evolution of a stoichiometric quantity of nitrogen, yields of products were determined by VPC analysis of the reaction mixtures. Products were isolated by preparative VPC and identified by comparison with reference compounds. **3**: IR (neat) 1700, 1649, 1630 cm^{-1}; NMR (CCl$_4$) δ 1.30 (t, 3 H), 1.93 (s, 3 H), 2.04 (s, 3 H), 4.18 (q, 2 H), 5.40–6.10 (m, 4 H). **4**: IR (neat) 1700, 1655, 1639 cm^{-1}; NMR (CCl$_4$) δ 1.30 (t, 3 H), 1.79 (s, 6 H), 4.18 (q, 2 H), 5.74 (s, 2 H), 5.99 (s, 2 H). **5**: IR (KBr disk) 3290, 1690 cm^{-1}; NMR (CCl$_4$) δ 1.30 (t, 3 H), 2.20 (s, 3 H), 2.31 (s, 3 H), 4.18 (q, 2 H), 6.10–6.23 (br s, 1 H), 6.78 (d, 1 H), 7.00 (d, 1 H), 7.70 (s, 1 H).

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