NOTES *Bull. Chem. Soc. Jpn.*, **55**, 2677—2678 (1982)

Ozonization of Organic Compounds. VI. Relative Reactivity of Protic Solvents toward Carbonyl Oxide

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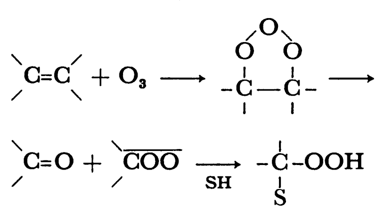
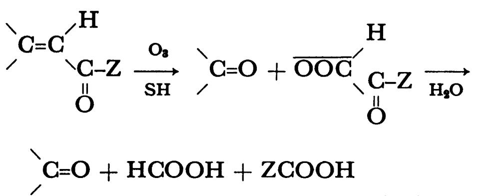
(Received October 8, 1981)

Synopsis. Tetramethylethylene was ozonized at 0 °C in several binary protic solvents and the relative reactivities of the solvents toward acetone carbonyl oxide were measured. The reactivity was found to decrease in the order methanol, ethanol, propyl alcohol, isopropyl alcohol, water, *t*-butyl alcohol, and acetic acid.

Carbonyl oxide is a key intermediate in the ozonolysis of olefinic compounds. It reacts with protic solvent (SH) to give hydroperoxide according to Eq. 1.[1] To understand the reactions of carbonyl oxide it is interesting and fundamental to know how the rate changes with solvents. For example, we reported previously[2] that the anomalous ozonolysis of *α,β*-unsaturated carbonyl compounds proceeded in protic solvents mainly by the rearrangement of carbonyl oxide substituted by carbonyl or carboxyl group (Eq. 2) and that the ratio of anomalous ozonolysis to total ozonolysis depend on the solvents. These results suggest that the rate of reaction of carbonyl oxide with protic solvent varies with solvents.



(1)

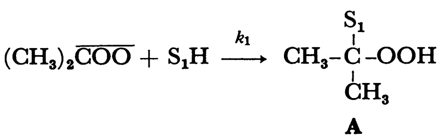


(2)

(Z=CH$_3$, OH)

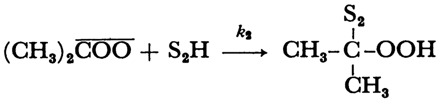
We wish to report here the relative reactivities of several protic solvents toward carbonyl oxide. We ozonized tetramethylethylene in binary protic solvents at 0 °C and measured the relative reactivities of protic solvents toward acetone carbonyl oxide, $(CH_3)_2\overline{COO}$ (Eqs. 3, 4).

The relative reactivity of S$_1$H and S$_2$H toward $(CH_3)_2\overline{COO}$, k_1/k_2, is expressed by Eq. 5 when the initial concentrations of S$_1$H and S$_2$H are high enough. It was difficult to measure the amounts of hydroperoxides **A** and **B** separately, so the relative reactivity k_1/k_2 was estimated from Eq. 6, where ΔS$_1$H and ΔS$_2$H represent the amount of S$_1$H and S$_2$H reacted, respectively.



$$(CH_3)_2\overline{COO} + S_1H \xrightarrow{k_1} CH_3\text{-}C(S_1)(CH_3)\text{-}OOH \qquad (3)$$

A



$$(CH_3)_2\overline{COO} + S_2H \xrightarrow{k_2} CH_3\text{-}C(S_2)(CH_3)\text{-}OOH \qquad (4)$$

B

$$\frac{k_1}{k_2} = \frac{\Delta A\cdot[S_2H]_0}{\Delta B\cdot[S_1H]_0} \qquad (5) \qquad\qquad \frac{k_1}{k_2} = \frac{\Delta S_1H\cdot[S_2H]_0}{\Delta S_2H\cdot[S_1H]_0} \qquad (6)$$

5 mmol of tetramethylethylene, S$_1$H, S$_2$H, and 15 ml of inactive solvent such as carbon tetrachloride, nitromethane, and ethyl methyl ketone were mixed in a reactor and O$_3$/O$_2$ gas was introduced into the reactor at 0 °C. Total amount of hydroperoxide was measured by iodometric titration. Both production of acetone and decrease of S$_1$H and S$_2$H were followed by GLC using PEG 20M, Porapak Q, and Apiezon Grease L columns. A part of tetramethylethylene was missed because of its high vapor pressure, so the amount of tetramethylethylene decreased was more than that of ozone introduced. Nevertheless, the ozonation was controlled so that some tetramethylethylene remained in the reaction mixture even at the end of ozonolysis in

TABLE 1. RELATIVE REACTIVITIES OF PROTIC SOLVENTS (S$_1$H AND S$_2$H) TOWARD CARBONYL OXIDE $(CH_3)_2\overline{COO}$ IN THE OZONOLYSIS OF 5 mmol OF TETRAMETHYLETHYLENE AT 0 °C

Run No.	1	2	3	4	5	6	7	8	9	10
S$_1$H	MeOH	MeOH	MeOH	MeOH	MeOH	EtOH	*n*-PrOH	*n*-PrOH	*n*-PrOH	*t*-BuOH
S$_2$H	EtOH	EtOH	*n*-PrOH	*i*-PrOH	H$_2$O	*n*-PrOH	*i*-PrOH	*t*-BuOH	AcOH	AcOH
Solvent[a)]	CH$_3$NO$_2$	CCl$_4$	CH$_3$NO$_2$	CH$_3$NO$_2$	MEK[b)]	CH$_3$NO$_2$	CCl$_4$	CCl$_4$	CCl$_4$	CCl$_4$
S$_1$H$_0$[c)] (mmol)	16.37	8.43	14.41	14.58	8.74	7.52	10.75	11.06	8.92	6.31
S$_2$H$_0$[c)] (mmol)	13.22	6.36	9.20	8.51	19.50	7.35	8.04	6.63	9.10	10.95
ΔS$_1$H (mmol)	1.85	1.40	1.48	1.40	1.05	0.89	0.76	1.64	1.46	0.85
ΔS$_2$H (mmol)	0.76	0.50	0.38	0.29	0.65[g)]	0.61	0.52	0.19	0.25	1.10
ΔSH[d)] (mmol)	2.61	1.90	1.74	1.69	1.70	1.50	1.28	1.83	1.71	1.95
ΔHPO[e)] (mmol)	2.36	1.85	1.84	1.40	1.65	1.46	1.40	1.93	1.85	1.90
k_1/k_2[f)]	2.0	2.1	2.5	2.8	3.6	1.4	1.1	5.2	6.0	1.3

a) 15 ml. b) Ethyl methyl ketone. c) Initial amounts of S$_1$H and S$_2$H in mmol. d) ΔSH=ΔS$_1$H+ΔS$_2$H.
e) Hydroperoxides. f) See text. g) Estimated by the amount of acetone formed.

Table 2. Polarity parameters and physical properties of protic solvents

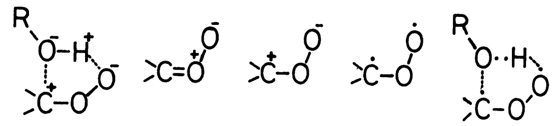
	E_T[a)]	Z[a)]	S[a)]	$pK_{auto}^{b)}$	BDE[c)]
MeOH	55.5	83.6	0.0499	17.20	104.4
EtOH	51.9	79.6	0.0000	18.88	104.2
n-PrOH	50.7	78.3	−0.0158	19.43	
i-PrOH	48.6	76.3	−0.0413	20.80	
t-BuOH	43.9	71.3	−0.1047	26.8	105.1
H_2O	63.1	94.6	0.1540	14.00	119
AcOH	51.2	79.2	0.0050	14.45	112

a) Empirical parameter of solvent polarity based on solvatochromism, Ref. 4. b) Autoprotolysis constants, Ref. 4. c) Bond dissociation energy of O–H bond in kcal/mol, Ref. 5.

order to avoid overozonization. Conversion of S_1H and S_2H was kept below 15%. It should be noted that α-methoxyalkyl hydroperoxide, $(CH_3)_2C(OCH_3)OOH$ decomposed to acetone quantitatively on GLC and that methanol was not detected.

It is necessary to confirm that the protic solvents react with carbonyl oxide quantitatively and peroxides, **A** and **B**, are the sole products in the reaction. As shown in Table 1, the amounts of peroxide formed (ΔHPO) and those of protic solvents reacted ($\Delta SH = \Delta S_1H + \Delta S_2H$) are in satisfactory agreement, which suggests that the hydroperoxides **A** and **B** are formed exclusively and that other peroxides such as diperoxide, triperoxide, and oligomers were not formed under the present conditions. It may be safely assumed that the inactive solvents used in Table 1 have little effect on the *relative* reactivities of protic solvents toward carbonyl oxides. From Table 1, the ratio $k_{MeOH}/k_{n\text{-}PrOH}$ is obtained as 2.5 in Run 3, which is in satisfactory agreement with the ratio calculated from the results of Runs 1 and 6, $2.0 \times 1.4 = 2.8$. Similarly, Run 4, and Runs 3 and 7 show that $k_{MeOH}/k_{i\text{-}PrOH}$ is 2.8.

Table 1 indicates that the reactivity of protic solvents toward $(CH_3)_2\overline{COO}$ decreased in the order of MeOH (1) > EtOH (0.50) > *n*-PrOH (0.40) > *i*-PrOH (0.36) > H_2O(0.28) > *t*-BuOH(0.077) > AcOH(0.063). The numbers in parentheses are the calculated reactivities of various protic solvents toward $(CH_3)_2\overline{COO}$ relative to methanol. The reactivity of alcohols has a close relation with the solvent polarity parameters, E_T, Z, S, and pK_{auto} as shown in Table 2. This suggests that the ionic transition state (**C**) plays an important role in the reaction of carbonyl oxide with protic solvent. In fact, the *ab initio* calculations[3)] for carbonyl oxide suggest that the zwitterions (**D**, **E**) are favored over biradical (**F**) in protic solvents. However, the low reactivities of water and acetic acid toward carbonyl oxide in spite of their strong protic character (Table 2) suggest that this is not the only factor that determines the reactivity. Table 2 also shows that the bond dissociation energies of O–H bonds of water and acetic acid are much larger than those of alcohols. This might imply some contribution of homolytic scission of O–H bond (**G**) as well as the ionic one. Recent report by Sawaki, Kato, and Ogata[6)] on the hydrogen atom abstraction by carbonyl oxide from toluene, cumene, and cyclohexane also suggests the importance of biradical character of carbonyl oxide.



C *D* *E* *F* *G*

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