Effects of Solvents on the Rate of Oxo Reaction of Methylacrylate

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While extensive studies on the effect of the structure of olefin and the partial pressure of carbon monoxide and hydrogen upon the rate of oxo reaction have been carried out, very little work on solvents in this regard has yet been done. Wender et al.[1], however, did study the effects of solvents on the oxo reaction rate of cyclohexene and established that the rate is increased only about 1.5 times in going from a saturated hydrocarbon to methanol; they therefore considered that highly polar intermediates may not be involved in the oxo reaction.

However, we have found that the effect of solvent on the rate of oxo reaction varies widely according to the olefin used[2]. For example, the oxo reaction rate of acrylonitrile in methanol at 120°C is about 6 times that in benzene. In this paper the author has investigated the effects of a variety of organic solvents and mixed solvents on the oxo reaction rate of methylacrylate. In addition, to obtain information on the mechanism of the effects of solvents, the rate of " base reaction " of Lewis base solvents such as methanol and acetone with dicobalt octacarbonyl, and the rate of formation of cobalt hydrocarbonyl from dicobalt octacarbonyl in toluene, methanol and acetone at 100°C and at 100 kg./cm^2 of 1 : 1 carbon monoxide and hydrogen, were measured.

Methylacrylate was chosen as the raw material for this study, because it gives a considerably wide variation in the effects of solvents and yields only one aldehyde, methyl-β-formylbutyrate. In addition, the oxo reaction of methylacrylate proceeds with scarcely any side reactions, because it gives a good yield of the aldehyde in every solvent.

Experimental

All of the solvents used were obtained in the best commercial grades available. These were treated with anhydrous sodium sulfate for 24 hr. and then distilled. The middle fraction consistent with the boiling point described in the literature was then collected in a dry flask, protected from atmospheric moisture. Methylacrylate was treated in the same way; its purity as determined by the morphorine method[3] was 98.5%.

Rates of the Oxo Reactions of Methylacrylate in Various Solvents.—The oxo reactions were carried out in a batch system by the same procedure as described in a preceding paper[4].

Thus, 150 ml. of the solvent containing 30.5 g. (350 mmol.) of methylacrylate and 0.60 g. (1.74 mmol.) of dicobalt octacarbonyl were put into a 300 ml. stainless steel rocking autoclave, and the autoclave was immediately filled with 1 : 1 synthesis gas to 200 kg./cm^2 and heated. After the temperature had risen to 120°C, the rocking was started, and the temperature was controlled at 120 ± 1°C. The rocking was continued until the pressure decrease stopped. The rate constant of the oxo reaction, k_a, was obtained from the following equation :

$$k_a=2.303\log\{(P_0-P_f)/(P_t-P_f)\}/t$$

where P_0 is the initial pressure at the reaction temperature, P_f is the pressure at the end of the reaction, and P_t is the pressure at time t.

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[1] I. Wender, S. Metlin, S. Ergun, H. W. Sternberg and H. Greenfield, *J. Am. Chem. Soc.*, **78**, 5401 (1956).

[2] H. Wakamatsu, R. Iwanaga and J. Kato, reported at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

[3] F. E. Critchfield, G. L. Funk and J. B. Johnson, *Anal. Chem.*, **28**, 76 (1956).

[4] R. Iwanaga, This Bulletin, **35**, 865 (1962).

Rates of "Base Reaction" of Solvents with $Co_2(CO)_8$.—Reactions were carried out at 20°C, and the rates were measured by the same procedure as described in a preceding paper⁵⁾. The rate constants of the base reaction, k_b, were obtained from the following equation;

$$k_b=2.303 \log \{[A^-]_f/([A^-]_f-[A^-]_t\}/t$$

where $[A^-]_f$ is the final amount of cobalt carbonyl anion, which corresponds to 2/3 mol. of the total cobalt in the $Co_2(CO)_8$ added, and $[A^-]_t$ is the amount of the anion at time t.

Initial Rates of Formation of Cobalt Hydrocarbonyl from $Co_2(CO)_8$ in Methanol and Acetone.—These were measured by the same technique as used in the measurement of the rate of formation of cobalt carbonyl anions from dicobalt octacarbonyl in the presence of amines⁴⁾. Namely, a crystal of 0.87 g. of dicobalt octacarbonyl was added to 100 ml. of methanol or of acetone after the temperature of the system had been raised to 100°C and the pressure of 1 : 1 carbon monoxide and hydrogen had been adjusted at 100 kg./cm², and the amount of cobalt hydrocarbonyl in an aliquot of the reaction solution was analyzed by the methylene blue method.

Results and Discussion

The rates of oxo reaction of methylacrylate in 17 organic solvents at 120°C and at the initial pressure of 260 kg./cm² of 1 : 1 carbon monoxide and hydrogen are listed in Table I, together with their dielectric constants and their rates of "base reaction" with dicobalt octacarbonyl at 20°C. An about eight-fold variation was observed between the fastest and slowest rates. As is illustrated by the data in Table I, no relationship between the rates of oxo reaction and the dielectric constants or the rate of base reaction could be found.

Benzene, toluene, ethylacetate and ethyl ether are considered to be inert in the oxo reaction. Therefore, the value of about 40×10^{-3} min⁻¹ may be considered a standard rate constant for the oxo reaction of methylacrylate; a value above it indicates a positive effect of the solvent, and a value below it indicates a negative effect of the solvent.

The rates in alcohols are very great except for the rate in *tert*-butanol. The large effects of alcohols may be explained by the same mechanism as proposed in the effect of pyridine⁴⁾, which involves the formation of an intermediate complex with cobalt carbonyl and the consequent rapid formation of cobalt hydrocarbonyl. This consideration agrees well with the observation that the formation of cobalt hydrocarbonyl in methanol is very rapid (cf. Table II).

The small positive effect of *tert*-butanol may be due to a steric hindrance, which may

TABLE I. RATES OF THE OXO REACTION OF METHYLACRYLATE IN VARIOUS SOLVENTS AT 120°C

Solvent	Rate constant $k_a\times10^3$ min⁻¹	Dielectric constant[a]	°C	Rate const. of base reaction[c] $k_b\times10^3$ min⁻¹
Benzene	41.8	2.284	20	—
Toluene	43.4	2.379	25	—
Ethylacetate	36.4	6.40	20[b]	9.9
Ethyl ether	41.2	4.335	20	—
Methanol	157	32.63	25	64.5
Ethanol	186	24.30	25	—
n-Butanol	167	17.8	20	13.8
Cyclohexanol	154	15.4	25	—
tert-Butanol	66.2	10.9	30	—
Acetone	59.5	20.7	25	57.5
Ethyl methyl ketone	39.1	15.45	20[b]	52.0
Tetrahydrofuran	57.1			47.2
Dioxane	27.4	2.235	25[b]	7.4
Acetic anhydride	30.2	20.7	19	—
Acetonitrile	77.2	37.5	20	196
Ethylene glycol	—	37.7	25	—
Formamide	—	109	20	—

a) The values were obtained from "American Institute of Physics Handbook", McGraw-Hill Co., New York (1957).

b) The values were obtained from C. Marden, "Solvents Manual", Cleaver-Hume Press Ltd., London (1954).

c) About 0.5 g. of $Co_2(CO)_8$ was reacted with 50 ml. of solvents at 20°C under atmospheric nitrogen.

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5) R. Iwanaga, ibid., 35, 247 (1962).

TABLE II. INITIAL RATES OF FORMATION OF $HCo(CO)_4$ IN TOLUENE, METHANOL AND ACETONE AT 100°C AND 100 kg./cm^2 OF 1 : 1 SYNTHESIS GAS

Solvent	Initial rate mol. % as Co per min.	Conversion at equilibrium %
Toluene	1.5	34
Acetone	3.2	29
Methanol	ca. 40	52

TABLE III. ANALYTICAL DATA OF A SOLUTION RESULTED FROM TREATMENT OF $Co_2(CO)_8$ IN ETHYLENE GLYCOL UNDER OXO CONDITION

		Found	Calcd.[a]
Total cobalt	mg./ml.	5.13	
Co in the product	mg./ml.	3.45	
Co(II) ion	mg./ml.	1.70	
Co/total Co	%	67.3	66.7
Co(II)/total Co	%	33.1	33.3

a) Calculated from the formula; $[Co(C_2H_6O_2)_3][Co(CO)_4]_2$

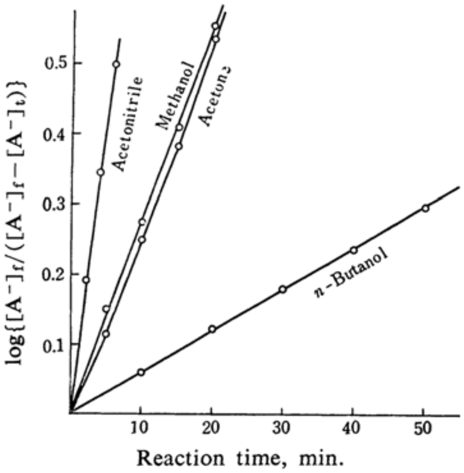

Fig. 1. Rates of the base reaction of dicobalt octacarbonyl with various Lewis bases.

occur in the complex formation with cobalt carbonyl, as described in the effect of 2,6-lutidine on the rate[4].

Acetone shows a moderate effect on the rate. Ethyl methyl ketone has an approximate standard value and is considered to be inert in the oxo reaction on the basis of its presumed steric factors.

In the case of the oxo reaction in acetonitrile, the original dark-brown solution changes to light yellow after the reaction is complete. This is probably due to the formation of amine by some hydrogenation of the nitrile.

In ethylene glycol, the oxo reaction did not take place. As is illustrated by Table III, it was found that dicobalt octacarbonyl reacts with ethylene glycol to form cobalt(II) ions and cobalt carbonyl anions even under the oxo condition, presumably according to Eq. 1.

$$3Co_2(CO)_8 + 6C_2H_6O_2 \rightarrow 2[Co(C_2H_6O_2)_3][Co(CO)_4]_2 + 8CO \quad (1)$$

Because the oxo reaction proceeds with no interference in benzene containing a small amount of ethylene glycol, as is shown in Fig. 2, it will be rather practical to explain the fact that the oxo reaction does not take place in ethylene glycol as follows: the complex salt consisting of a cobalt-ethylene glycol cation and a cobalt carbonyl anion has been produced by the base reaction before the pressure and temperature are raised to the oxo reaction condition, and the salt, once produced, is too stable in a higher polar solvent such as ethylene glycol to be converted to dicobalt octacarbonyl or cobalt hydrocarbonyl. It may be due to the same reason why the oxo reaction does not take place in formamide.

As is illustrated in Fig. 3, the rate is decreased by increasing the amount of water in the methanol. When 15 vol.% or more of water was added to the methanol, the reaction

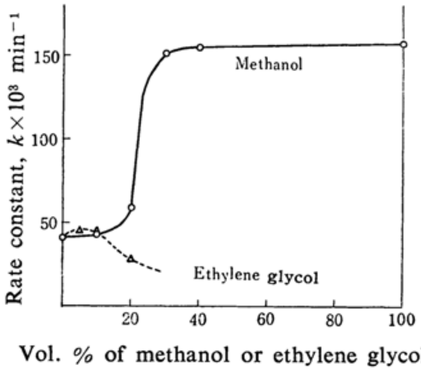

Fig. 2. Rates of the oxo reaction of methylacrylate in mixed solvent of benzene and methanol or ethylene glycol.

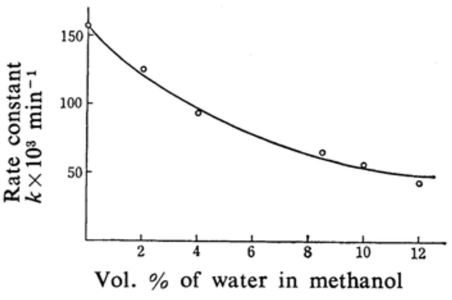

Fig. 3. Effects of water content in methanol as solvent of the oxo reaction of methylacrylate.

did not take place. This negative effect of water may be explained in terms of the dissociation of the cobalt hydrocarbonyl presumed to be a catalyst of the oxo reaction, because it is known that cobalt hydrocarbonyl dissociates completely in water at 26°C[6].

Summary

The rates of methylacrylate oxo reactions in a variety of organic solvents were measured by a batch system at 120°C. In general, the rate varies widely in the following order: alcohols $>$ acetone $>$ toluene; this order did not correspond with the order of their dielectric constants nor with the rates of their "base reactions" with dicobalt octacarbonyl, but it does agree with the order of their rates of formation of cobalt hydrocarbonyl under oxo conditions. *tert*-Butanol shows a positive but small effect on the rate as compared with toluene. When ethylene glycol and formamide having higher dielectric constants were used as solvents, the oxo reaction did not take place. On the bases of these results the mechanisms of the effects of the solvents have been discussed.

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[6] H. W. Sternberg, I. Wender, R. A. Friedel and M. Orchin, *J. Am. Chem. Soc.*, 75, 2717 (1953).