Table I. Attempted Fitting of Variations in f[a]

[NaOH]	surfactant	K_S, M^{-1}	β_0	K_{Br}^{OH}	K_B^M [b]	plot[c]
0.01	1	200	0.75	15	0.05	1
		200	0.75	5	0.12	
		200	0.85	5	0.15	
0.01	1/CTABr[d]	300	0.75	15	0.12 (0.12)	2
		300	0.85	15	0.17	
0.1	1	400	0.75	15	0.025	3
		400	0.75	4	0.06	4
		400	0.85	4	0.08	
0.1	1/CTABr[d]	400	0.75	15	0.14 (0.16)	5

[a] Calculated taking cmc = 6×10^{-4} M except for comicelles in 0.01 M NaOH where cmc = 10^{-3} M. [b] Values in parentheses calculated with constant β. [c] Refers to curves in Figure 1. [d] [1]:[CTABr], 1:10.

but surfactant concentrations are such that the calculations are insensitive to the value of the cmc.

Plots of f vs. [surfactant] are shown in Figure 1. They are based on the parameters given in Table I. For deprotonation in 0.1 M NaOH and comicelles of 1 and CTABr the experimental data can be fitted taking values of K_S, K_{Br}^{OH} and K_B^M which are very similar to those used to fit the data in CTABr,[9a] and the fitting is insensitive to variation of β (eq 7). However, for deprotonation in micelles of the hydroxyethyl surfactant 1 we could not fit the data taking values of both K_{Br}^{OH} and K_B^M similar to those which fit the data in CTABr (Figure 1 and Table I).

We were unable to fit the data for deprotonation in 0.01 M NaOH, although the deviations are not large for comicelles of 1 and CTABr. However, for micelles of 1 we could not fit the data even approximately by using parameters similar to those used for data in CTABr, and we had to take a lower than expected value of K_S.[9a] As is often found for experiments in ionic aqueous micelles various combinations of parameters give very similar calculated plots.

The ion-exchange model relies on the value of β,[6] which is subject to uncertainty, because of changes in extent of deprotonation, but the uncertainty should be relatively small for comicelles of 1 and CTABr. There is also uncertainty as to the depletion of OH^- by deprotonation of the hydroxyl group of 1, with formation of **1a**. The alkoxide residue in **1a** should be too weakly basic to deprotonate 5-nitroindole. An additional question is that of micellar binding of the anionic conjugate base of the indicator. Binding to nonfunctional micelles was assumed to be essentially quantitative,[8,9] although this assumption probably fails in relatively concentrated salt solutions. It may also fail as the charge on micellized 1 decreases due to formation of zwitterionic **1a**. Thus our assumption of complete binding of the anion of 5-nitroindole will be least satisfactory at relatively low [1] where there will be most deprotonation of the hydroxy group of the surfactant. However, incomplete binding is not the only source of the discrepancies because if it were they would be most serious at high [NaOH].

It appears that the pseudophase ion-exchange model cannot be applied quantitatively to deprotonation of 5-nitroindole in solutions of micellized 1, although it is qualitatively satisfactory in that it explains the decrease of f with increasing [1] and the relatively small increase of f with increasing [NaOH].

The pseudophase model of micellar effects upon reaction rates and equilibria is based on the assumption that the micellar reaction takes place in a discrete region adjacent to the ionic head groups, so that the problem is to estimate reactant concentrations in this region.[2-7] Apparently this model cannot be readily applied to a cationic micelle which becomes zwitterionic as the hydroxyl group is deprotonated, and this changing charge distribution is not adequately described merely by a decrease in β.

Table II. Deprotonation of 5-Nitroindole-2-carboxylate Ion[a]

	conditions			
	0.01 M NaOH		0.1 M NaOH	
[D], M	1	1/CTABr[b]	1	1/CTABr[b]
0.01	20 (24)	21 (25)	39 (43)	51 (53)
0.02	17 (21)	16 (20)	35 (39)	42 (45)
0.03	15 (20)	15 (19)	32 (36)	38 (41)
0.04	14 (19)	14 (18)	30 (34)	35 (38)
0.05	14 (19)	13 (17)	29 (33)	33 (36)

[a] Values of f% estimated from absorbance at 393 nm; values in parentheses are from absorbance at 387 nm. [b] Comicelles of [1]:[CTABr], 1:10.

The extent of deprotonation of 5-nitroindole-2-carboxylate ion decreases, as expected, with increasing [surfactant] but the values depend upon the wavelength used for estimation of f (Table II). This problem was not found for experiments with CTABr,[9b] but in solutions containing 1 there is only an ill-defined shoulder in the spectrum of the indicator, whereas it is well-defined in CTABr. Such spectral shifts in micellar solutions are sometimes observed and can be a problem in measurements of acid dissociation constants.[18]

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Registry No. 1, 20317-32-2; BH, 6146-52-7; CTAB, 57-09-0.

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Conversion of Formaldehyde to Acetic Acid. Formic Acid as a Stoichiometric CO Substitute

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We recently reported[1] the reactions in eq 1 and 2. In the course of that work we found that the reaction of formaldehyde with 65% aqueous HI and 500 psi of CO at 100 °C results in its quantitative conversion to CH_3CO_2H.[2]

$$CO \xrightarrow{HI,\ H_2O} CH_3CO_2H \qquad (1)$$

$$CH_3CO_2H + CO \xrightarrow{HI,\ H_2O} CH_3CH_2CO_2H \qquad (2)$$

Since these are elementary transformations that involve simple organic molecules, we regard this chemistry as being basic. However, in this and in an extensive body of other chemistry of carbon monoxide, rather high pressures can be required. A variant of this chemistry that could be effected under ordinary laboratory conditions would therefore be quite useful.

The Koch–Haaf reaction[3] involves the use of HCO_2H, the hydrate of CO, in substantial excess as a substitute for

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Table I. Reactions of Formaldehyde in Aqueous HX

present before reaction[a]			reaction conditions		present after reaction, %		
formaldehyde	HCO_2H	solvent	temp. °C	time, h	CH_3CO_2H[b]	CH_3I[b]	HCO_2H[c]
(1.0)	1.0	65% HI	~105	24	76	6	18
(1.0)	1.2	65% HI	~105	24	90	5	33
(1.0)[d]	1.0	65% HI	~130	4.5	83	7	trace
(1.0)	1.2	65% HI	~130	4.5	93	5	9
(1.0)	1.0	43% HI	~130	4.5	12	12	83
1.0		65% HI	~130	4.5	12	12	
1.0		65% HI	~160	1	12	11	
1.0		43% HI	~130	4.5		15	31[b]
(1.0)	1.0	37% HCl	~130	4.5	60[e]		

[a] Amounts given are relative. [b] Based on formaldehyde. [c] Based on HCO_2H, unless noted otherwise. [d] Use of CH_3CO_2H instead of formaldehyde resulted in quantitative recovery of the CH_3CO_2H; use of CH_3OH instead of formaldehyde resulted in no production of CH_3CO_2H. [e] The product is $ClCH_2CO_2H$. CAUTION: CH_3OCH_2Cl and $ClCH_2OCH_2Cl$ are carcinogens.

CO and yields carboxylic acids from substrates that can produce carbonium ions. Reports of the use of *stoichiometric* quantities of formic acid to convert alcohols to ^{13}C-labeled carboxylic acids[4a] and paraformaldehyde to glycolic acid and its polymers[4b] stimulated us to think of the possibility that HCO_2H could be a useful and practical substitute for CO in reactions that we had reported and more generally.

We have now found that reaction of formaldehyde with a stoichiometric amount of formic acid in aqueous HI gives acetic acid in high yield (eq 3) and that formaldehyde alone also yields some acetic acid (eq 4). Some representative

$$\text{formaldehyde} + HCO_2H \xrightarrow{HI,\ H_2O} CH_3CO_2H \quad (3)$$

$$\text{formaldehyde} \xrightarrow{HI,\ H_2O} CH_3CO_2H \quad (4)$$

results are in Table I.[5] We anticipate the utility of near-equivalent amounts of HCO_2H, introduced as such or formed in situ, as a substitute for CO in a wide variety of reactions.

In addition, we have found the also new, but less novel, reaction in eq 5 (Table I), a reaction that may model the first portion of the pathway operative in aqueous HI.

$$\text{formaldehyde} + HCO_2H \xrightarrow{HCl,\ H_2O} ClCH_2CO_2H \quad (5)$$

Experimental Section

All materials were of commercial origin. The 65% HI was obtained from Fluka; 43% HI is 65% HI that has been diluted with an equal volume of water.

^{1}H and ^{13}C NMR spectra were recorded on Varian A-60A and XL-200 spectrometers, respectively.

The initial reaction mixtures (1 mmol of formaldehyde as trioxane,[6a] 0.40 mL of solvent, other reagents as indicated in Table I) were sealed under vacuum in 4-mm i.d., 5- or 6-mm o.d. Pyrex tubes.[6b] They were heated in an oven under the conditions specified in Table I.

Final reaction mixtures were similar to those encountered earlier.[1] They were monitored and analyzed by use of NMR spectroscopy. Any opening of a tube was done after it had been cooled in liquid nitrogen; it was then fitted with a serum cap while at that temperature and any transfers were made through the cap by use of a gas-tight syringe after the mixture had warmed to room temperature. Since the product CH_3I was incompletely miscible with the aqueous HI, the reaction mixture was treated with benzene to facilitate analysis for CH_3I.

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Registry No. HCO_2H, 64-18-6; CH_3CO_2H, 64-19-7; $ClCH_2CO_2H$, 79-11-8; formaldehyde, 50-00-0.

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(6) (a) α-Polyoxymethylene also exhibits this chemistry. (b) The reaction proceeds well also when run in an open system.

A Detailed, Convenient Preparation of Dimethyl 1,2,4,5-Tetrazine-3,6-dicarboxylate

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In the course of recent studies[2] we required substantial quantities of dimethyl 1,2,4,5-tetrazine-3,6-dicarboxylate (1), an electron-deficient heterocyclic aza diene especially suited for inverse electron demand ($LUMO_{diene}$ controlled) Diels–Alder reactions with electron-rich dienophiles and heterodienophiles,[3] and have developed an optimal, im-

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