

Physical Organic Chemistry of Transition Metal Carbene Complexes. 5.¹ Kinetics and Mechanism of Hydrolysis of (CO)₅Cr=C(OCH₃)CH₃ and (CO)₅Cr=C(OCH₂CH₃)CH₃ in Aqueous Acetonitrile

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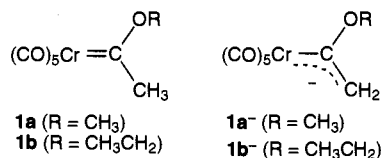
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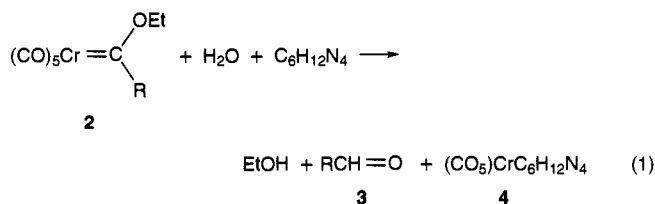
Abstract: This paper reports a product and kinetic study of the hydrolysis of (CO)₅Cr=C(OCH₃)CH₃ (**1a**) and (CO)₅Cr=C(OCH₂CH₃)CH₃ (**1b**) in 50% aqueous acetonitrile at 25 °C. The organic products are acetaldehyde and methanol in the case of **1a** and acetaldehyde and ethanol in the case of **1b**. The reactions are general base catalyzed and subject to a primary solvent kinetic isotope effect. This indicates a mechanism which includes a rate limiting proton transfer. A number of plausible mechanisms which are consistent with the experimental data are scrutinized. The preferred mechanism involves rapid deprotonation of the methyl group of the carbene complexes to form **1a⁻** or **1b⁻**, respectively, followed by rate limiting Cr-C bond cleavage of **1a⁻** (**1b⁻**) concerted with protonation on the carbene carbon to yield (CO)₅Cr(CH₂=CHOR), which is rapidly hydrolyzed to the final products.

Introduction

(Methoxymethylcarbene)pentacarbonylchromium(0) (**1a**) and (ethoxymethylcarbene)pentacarbonylchromium(0) (**1b**)



are prototypical transition metal carbene complexes or "Fischer carbenes".² In view of their prominence it is surprising that no kinetic study of their hydrolysis has been reported. In fact, the hydrolysis of Fischer carbenes in general has thus far received very little attention. Only recently Aumann et al.³ have reported a product study of the hydrolysis of several Fischer carbenes of the type **2** (R = Ph, CH=CHPh, C₄H₃S, CH=CHC₄H₃S, and C≡CPh) in THF containing small quantities of water. In



the presence of the tricyclic amine urotropine (C₆H₁₂N₄),⁴ the aldehyde **3** is formed in ≥90% yield with all R groups except when R is C≡CPh; in this latter case, the triple bond undergoes nucleophilic attack by the amine.

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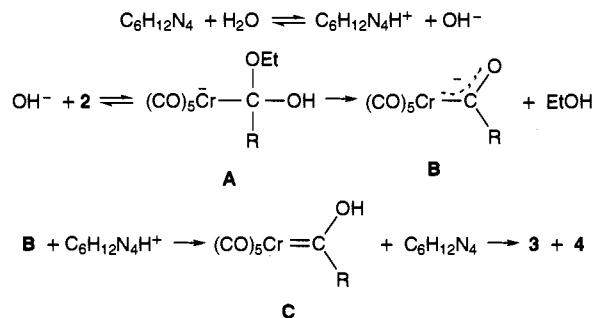
(1) Part 4: Bernasconi, C. F.; Flores, F. X.; Gandler, J. R.; Leyes, A. E. *Organometallics* **1994**, *13*, 2186.

(2) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, I. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1983.

(3) Aumann, R.; Hinterding, P.; Krüger, C.; Goddard, R. *J. Organomet. Chem.* **1993**, *459*, 145.

(4) Hexamethylenetetramine.

Scheme 1



As to a possible mechanism for eq 1 the authors suggested Scheme 1, but no details with respect to the last step were given except to refer to Fischer and Massböl,⁵ who have shown that **C** easily breaks down to the corresponding aldehyde.

The hydrolysis of **1a** or **1b** could conceivably proceed by a similar mechanism although the relatively facile deprotonation of these compounds, to form the corresponding anions **1a⁻** (pK_a(**1a**) = 12.50)^{6,7} and **1b⁻** (pK_a(**1b**) = 12.97),^{6,8} may open up another reaction channel, as shown in eq 2 where **B** may be OH⁻ or a buffer base. The reaction of eq 2 is analogous to



that postulated for the formation of vinyl ethers from various (alkylmethoxycarbene)pentacarbonylchromium(0) complexes in the presence of neat pyridine and *N*-methylmorpholine, or of quinuclidine in hexane,⁹ and the formation of 2,3-dihydrofuran in the thermal decomposition of (2-oxacyclopentylidene)pentacarbonylchromium(0) in pyridine.¹⁰

(5) Fischer, E. O.; Massböl, A. *Chem. Ber.* **1967**, *100*, 2445.

(6) In 50% CH₃CN-50% water at 25 °C.

(7) Bernasconi, C. F.; Sun, W. *J. Am. Chem. Soc.* **1993**, *115*, 12526.

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(9) (a) Fischer, E. O.; Massböl, A. *J. Organomet. Chem.* **1968**, *12*, P15.

(b) Fischer, E. O.; Plabst, W. *Chem. Ber.* **1974**, *107*, 3326.

(10) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895.

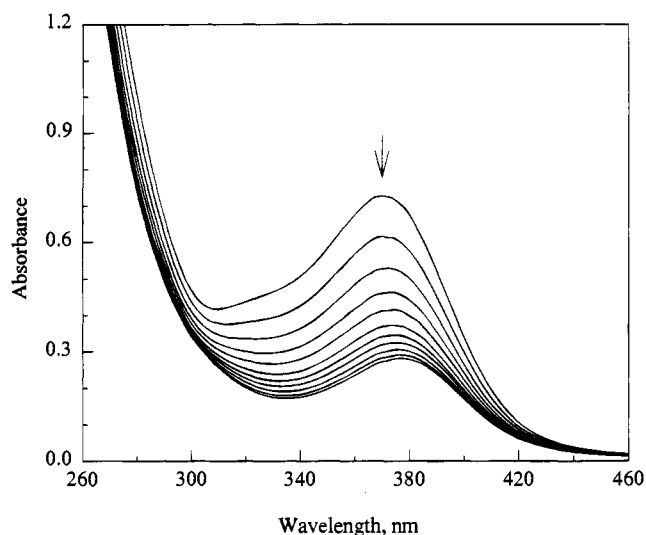


Figure 1. Hydrolysis of **1b** in 50% CH₃CN–50% water at 25 °C, [**1b**]₀ = 1.1 × 10⁻⁴ M, pH 11.97. First spectrum taken immediately after mixing, subsequent spectra taken at 18-s intervals.

In this paper we describe a product and kinetic study of the hydrolysis of **1a** and **1b** in 50% acetonitrile–50% water (v/v). In agreement with Aumann's³ results, the organic products will be shown to be acetaldehyde and methanol (**1a**) or ethanol (**1b**), respectively. However, none of the mechanistic possibilities that are consistent with our kinetic results conform to Scheme 1.

Results

General Features and Product Study. All experiments were carried out in 50% acetonitrile–50% water (v/v). When **1a** or **1b** is placed into a KOH solution, two reactions are observed by monitoring the UV/vis spectrum. The faster of the two is in the millisecond range and refers to the deprotonation that leads to the respective anions **1a**⁻ and **1b**⁻. A detailed account of this process has been published recently for **1a**,⁷ and a similar report will be published shortly for **1b**.⁸

The second process occurs on a time scale of seconds at high pH but becomes progressively slower as the pH is decreased. Figure 1 shows time resolved absorption spectra of the reaction of **1b** at pH 11.97. At this pH the proton transfer equilibrium between **1b** and **1b**⁻ strongly favors the un-ionized form, **1b**, whose pK_a is 12.98.⁸ Hence the spectra in Figure 1 represent the conversion of **1b** to hydrolysis products. The final spectrum shows the presence of (CO)₅CrOH⁻, or a mixture of (CO)₅CrOH⁻ and (CO)₅Cr(CH₃CN); this was confirmed (a) by comparison with the spectrum of a solution of (CO)₅CrOH⁻/(CO)₅Cr(CH₃CN) independently prepared by irradiating Cr(CO)₆ in aqueous acetonitrile/KOH and (b) by HPLC analysis of the product solution and of the authentic (CO)₅CrOH⁻/(CO)₅Cr(CH₃CN) solution.

The organic products of the hydrolysis reactions are acetaldehyde and methanol in the case of **1a** and acetaldehyde and ethanol in the case of **1b**. They were identified by ¹H NMR and showed yields higher than 90%. There were minor, unidentified byproducts but no detectable amounts of methyl vinyl ether (reaction of **1a**) or ethyl vinyl ether (reaction of **1b**) that could conceivably have been formed via eq 2.

The possibility that the hydrolysis of **1a** or **1b** initially leads to the corresponding vinyl ether (eq 2) which is subsequently hydrolyzed to acetaldehyde and the corresponding alcohol was further tested as follows. Ethyl vinyl ether was treated with 0.01 M KOH which corresponds to a typical reaction condition

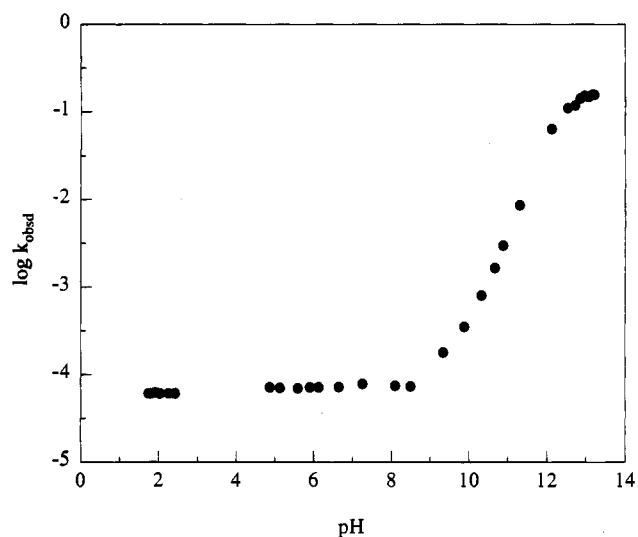


Figure 2. pH–rate profile of the hydrolysis of **1a** in 50% CH₃CN–50% water at 25 °C.

in the hydrolysis of **1b**. In the absence of any other additive, no organic material except for ethyl vinyl ether could be detected even after 144 h at 25 °C and 48 h at 45 °C. However, when (CO)₅Cr(CH₃CN), generated by UV irradiation of Cr(CO)₆ in acetonitrile, was added, approximately 40% of the ethyl vinyl ether was converted to acetaldehyde. Since in these experiments the ethyl vinyl ether was used in a 6.5-fold excess over Cr(CO)₆, the yield based on this latter is about 260%, which indicates that Cr(CO)₅ acts catalytically.

Kinetics. All runs were conducted under pseudo-first-order conditions with the carbene complex as the minor component. The temperature was 25 °C and the ionic strength was maintained at 0.1 M with KCl. Figure 2 shows an extended pH–rate profile for the hydrolysis of **1a**. *k*_{obsd}, the pseudo-first-order rate constant, was determined in KOH solution, in dilute borate, *N*-methylmorpholine, and acetate buffers, and in HCl solutions.

The *k*_{obsd} values determined in buffer solutions showed a small dependence on buffer concentration, indicating general base catalysis. The *k*_{obsd} values plotted in Figure 2 represent extrapolations to zero buffer concentrations. The slopes of the buffer plots provided *k*_B values (3.1 × 10⁻³ M⁻¹ s⁻¹ for borate, 3.5 × 10⁻³ M⁻¹ s⁻¹ for *N*-methylmorpholine, and 8.7 × 10⁻³ M⁻¹ s⁻¹ for acetate ion) for general base catalysis. Because the emphasis in these experiments was on getting accurate extrapolated *k*_{obsd} values at zero buffer concentration, the buffer concentrations and their range were quite limited ([B] ≤ 0.01 M) and hence the *k*_B values should be regarded as approximate.

We also performed a more limited study, restricted to KOH solutions, of the hydrolysis of **1b**. The results are shown in Figure 3.

A number of experiments were carried out in 50% acetonitrile–50% D₂O aimed at determining the kinetic solvent isotope effect. The results are summarized in Table 1. For **1a** all measurements were carried out at pH ≫ pK_a^{CH}, i.e., in the high plateau region of the pH–rate profile (Figure 2). For **1b** the first two entries refer to pH values ≪ pK_a^{CH}, which corresponds to the sloping part of the pH–rate profile; hence the *k*_{obsd}(H₂O)/*k*_{obsd}(D₂O) ratio is relatively small. The last two entries where the isotope effect is large were obtained in the plateau region, i.e., at pH ≫ pK_a^{CH}. For the third entry the *k*_{obsd}(H₂O)/*k*_{obsd}(D₂O) ratio is somewhat higher than for the first two entries; this reflects the fact that pH < pK_a^{CH} instead of pH ≪ pK_a^{CH}.

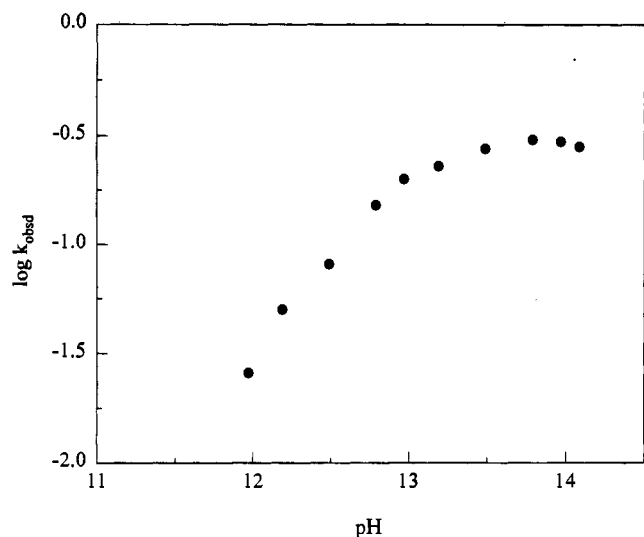


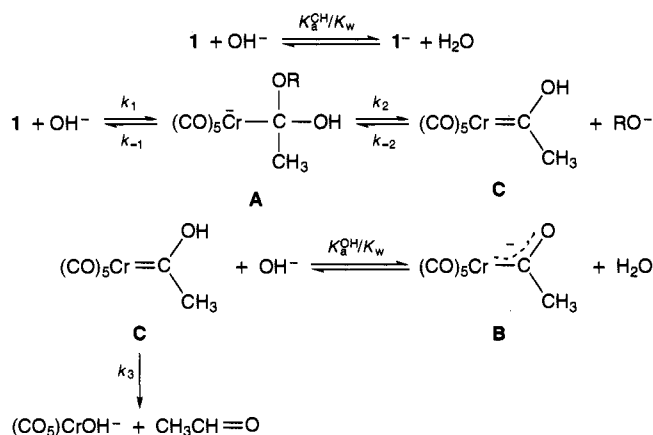
Figure 3. pH-rate profile of the hydrolysis of **1b** in 50% CH₃CN–50% water at 25 °C.

Table 1. Kinetic Solvent Isotope Effect in the Hydrolysis of **1a** and **1b** in 50% CH₃CN–50% Water at 25 °C^a

[KOL], M	$k_{\text{obsd}}(\text{H}_2\text{O}), \text{s}^{-1}$	$k_{\text{obsd}}(\text{D}_2\text{O}), \text{s}^{-1}$	$k_{\text{obsd}}(\text{H}_2\text{O})/k_{\text{obsd}}(\text{D}_2\text{O})$
1a			
0.01	1.69×10^{-1}	4.41×10^{-2}	3.83
0.02	1.53×10^{-1}	4.09×10^{-2}	3.74
0.03	1.63×10^{-1}	3.92×10^{-2}	4.16
0.04	1.52×10^{-1}	3.66×10^{-2}	4.15
1b			
0.0006	2.60×10^{-2}	1.26×10^{-2}	2.06
0.001	5.00×10^{-2}	2.34×10^{-2}	2.14
0.002	8.20×10^{-2}	2.91×10^{-2}	2.82
0.06	2.94×10^{-1}	4.16×10^{-2}	7.06
0.08	2.83×10^{-1}	4.13×10^{-2}	6.85

^a $\mu = 0.1 \text{ M (KCl)}$.

Scheme 2



Discussion

The principal objective of this study was to establish the mechanism of hydrolysis of **1a** and **1b** in aqueous acetonitrile. In view of the fact that the products (aldehyde and alcohol) are the same as those by Aumann et al.³ in eq 1, we need to examine whether a mechanism similar to that proposed by Aumann (Scheme 1) could explain our results. Scheme 2 shows this mechanism adapted to the OH⁻-promoted hydrolysis of **1a** or **1b**; note that the scheme includes the deprotonation of **1** as preequilibrium (K_w is the self-ionization constant of the solvent) and implies, more reasonably, that **C** is formed directly by loss of RO⁻ from **A** rather than indirectly by loss of ROH from **A** and subsequent protonation of **B**.

With respect to Scheme 2, three special cases need to be considered.

(1) **Rate Limiting k_1 Step.** For this case k_{obsd} is given by eq 3 which is consistent with the observed pH-rate profiles.

$$k_{\text{obsd}} = \frac{k_1[\text{OH}^-]}{1 + \frac{K_a^{\text{CH}}}{K_w}[\text{OH}^-]} \quad (3)$$

Equation 3 simplifies to eq 4 at pH $\ll \text{p}K_a^{\text{CH}}$ and to eq 5 at pH

$$k_{\text{obsd}} = k_1[\text{OH}^-] \quad (4)$$

$$k_{\text{obsd}} = k_1 K_w / K_a^{\text{CH}} \quad (5)$$

$\gg \text{p}K_a^{\text{CH}}$, while the break in the pH-rate profile occurs at pH = $\text{p}K_a^{\text{CH}}$. This break occurs at pH $\approx 12.35 \pm 0.15$ for **1a** and pH $\approx 12.80 \pm 0.15$ for **1b**, consistent with the kinetically determined $\text{p}K_a = 12.50$ for **1a**⁷ and 12.97 for **1b**.⁸

(2) **Rate Limiting k_2 Step.** If **A** is a non-accumulating intermediate and k_2 is rate limiting, k_{obsd} is given by eq 6 with $K_1 = k_1/k_{-1}$. pH $\ll \text{p}K_a^{\text{CH}}$ eq 6 becomes eq 7 and at pH \gg

$$k_{\text{obsd}} = \frac{K_1 k_2 [\text{OH}^-]}{1 + \frac{K_a^{\text{CH}}}{K_w} [\text{OH}^-]} \quad (6)$$

$\text{p}K_a^{\text{CH}}$ it simplifies to eq 8; the break occurs again at pH = $\text{p}K_a^{\text{CH}}$.

$$k_{\text{obsd}} = K_1 k_2 [\text{OH}^-] \quad (7)$$

$$k_{\text{obsd}} = K_1 K_w k_2 / K_a^{\text{CH}} \quad (8)$$

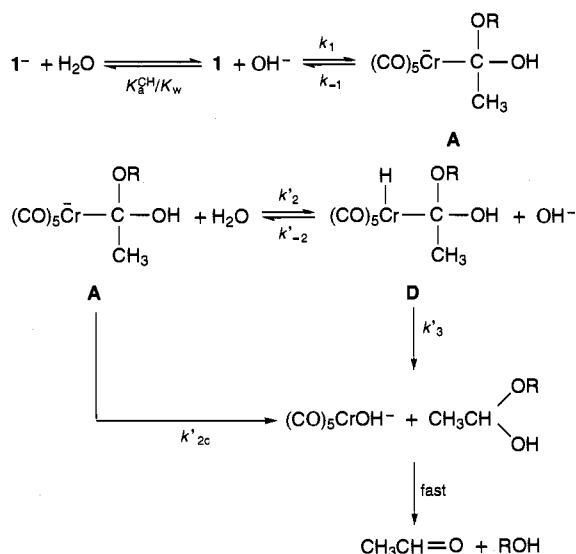
The problem with cases 1 and 2 is that they do not account for the observed kinetic solvent isotope effects (Table 1). The $k_{\text{obsd}}(\text{H}_2\text{O})/k_{\text{obsd}}(\text{D}_2\text{O})$ ratios are of a magnitude consistent with a primary kinetic isotope effect, implying a rate limiting proton transfer. However, neither the k_1 nor the k_2 step involve such a proton transfer and hence this mechanism must be rejected. This is most clearly seen from the $k_{\text{obsd}}(\text{H}_2\text{O})/k_{\text{obsd}}(\text{D}_2\text{O})$ ratios in the pH-dependent part of the pH-rate profile where eq 4 (k_1 rate limiting) or eq 7 (k_2 rate limiting) would have to be invoked. Inasmuch as OD⁻ is a stronger base and better nucleophile than OH⁻,¹¹ both k_1 and K_1 should be larger in D₂O than in H₂O, which should manifest itself in a $k_{\text{obsd}}(\text{H}_2\text{O})/k_{\text{obsd}}(\text{D}_2\text{O})$ ratio that is *smaller*, not larger, than unity.

(3) **Rate Limiting k_3 Step.** This case can be rejected on the grounds that the reaction would no longer follow first-order kinetics because the concentration of RO⁻, which is a byproduct in the formation of **C**, would increase with time and hence slow down the reaction by the law of mass action. Furthermore, in aqueous acetonitrile, RO⁻ is immediately converted to ROH + OH⁻, which means that the k_2 step cannot be considered truly reversible.

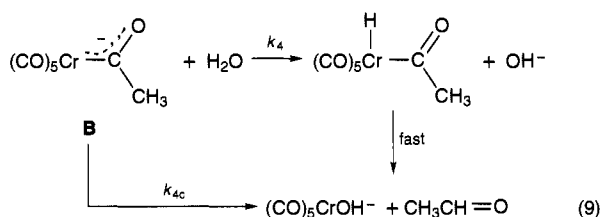
A modification of Scheme 2 in which the product forming reaction involves rate limiting protonation of the acylate ion (**B**) on the metal followed by rapid reductive elimination (eq

(11) (a) Laughton, P. M.; Robertson, R. E. In *Solute-Solvent Interactions*; Coetzee, J. F., Ritchie, C. D., Eds.; Dekker: New York, 1969; p 400. (b) Schowen, R. L. *Prog. Phys. Org. Chem.* **1972**, *9*, 275.

Scheme 3



9), or possibly rate limiting carbon protonation of **B** concerted



with Cr–C bond cleavage, to lead directly to acetaldehyde (k_{4c} in eq 9), is, in principle, consistent with the observed kinetic isotope effect. However, this version of Scheme 2 can be rejected for the same reasons as case 3 above.

An alternative mechanism that includes initial nucleophilic attack on the carbene carbon by OH^- and is consistent with all experimental observations is shown in Scheme 3. Assuming that **A** does not accumulate to detectable levels and that conversion of **A** to the hemiacetal is stepwise, with the k'_2 -step being rate limiting, k_{obsd} is given by eq 10 which is of the same

$$k_{\text{obsd}} = \frac{K_1 k'_2 [\text{OH}^-]}{1 + \frac{K_a^{\text{CH}}}{K_w} [\text{OH}^-]} \quad (10)$$

mathematical form as eq 6. Hence the limiting expressions at $\text{pH} \ll \text{p}K_a^{\text{CH}}$ and $\text{pH} \gg \text{p}K_a^{\text{CH}}$ are given by eqs 11 and 12, respectively. For the variation in which protonation of the

$$k_{\text{obsd}} = K_1 k'_2 [\text{OH}^-] \quad (11)$$

$$k_{\text{obsd}} = K_1 K_w k'_2 / K_a^{\text{CH}} \quad (12)$$

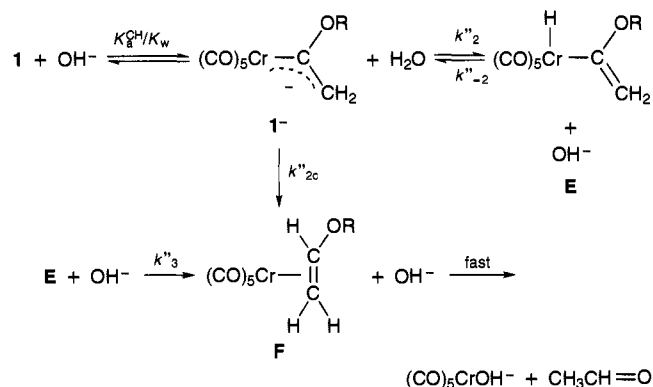
tetrahedral carbon is concerted with cleavage of the Cr–C bond, k'_2 in eqs 10–12 is substituted by k'_{2c} .

Equations 11 and 12 are consistent with the $k_{\text{obsd}}(\text{H}_2\text{O})/k_{\text{obsd}}(\text{D}_2\text{O})$ ratios. At $\text{pH} \ll \text{p}K_a^{\text{CH}}$, this ratio becomes

$$\frac{k_{\text{obsd}}(\text{H}_2\text{O})}{k_{\text{obsd}}(\text{D}_2\text{O})} = \frac{K_1(\text{H}_2\text{O}) k'_2(\text{H}_2\text{O})}{K_1(\text{D}_2\text{O}) k'_2(\text{D}_2\text{O})} \quad (13)$$

Here the primary isotope effect of the rate limiting step, k'_2 ($\text{H}_2\text{O})/k'_2(\text{D}_2\text{O})$, is attenuated by the $K_1(\text{H}_2\text{O})/K_1(\text{D}_2\text{O})$ ratio

Scheme 4

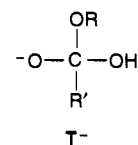


which is expected to be $< 1^{11}$ and explains why $k_{\text{obsd}}(\text{H}_2\text{O})/k_{\text{obsd}}(\text{D}_2\text{O})$ is only approximately 2 (first two entries for **1b** in Table 1). At $\text{pH} \gg \text{p}K_a^{\text{CH}}$ the ratio becomes

$$\frac{k_{\text{obsd}}(\text{H}_2\text{O})}{k_{\text{obsd}}(\text{D}_2\text{O})} = \frac{K_1(\text{H}_2\text{O}) K_w(\text{H}_2\text{O}) K_a^{\text{CH}}(\text{D}_2\text{O}) k'_2(\text{H}_2\text{O})}{K_1(\text{D}_2\text{O}) K_w(\text{D}_2\text{O}) K_a^{\text{CH}}(\text{H}_2\text{O}) k'_2(\text{D}_2\text{O})} \quad (14)$$

Here the product $\{K_w(\text{H}_2\text{O})/K_w(\text{D}_2\text{O})\} \{K_a^{\text{CH}}(\text{D}_2\text{O})/K_a^{\text{CH}}(\text{H}_2\text{O})\}$ is expected to be larger than unity¹¹ and to compensate, or overcompensate, for the $K_1(\text{H}_2\text{O})/K_1(\text{D}_2\text{O})$ ratio (< 1), which explains why the solvent isotope effect at $\text{pH} \gg \text{p}K_a^{\text{CH}}$ is substantially larger than that at $\text{pH} \ll \text{p}K_a^{\text{CH}}$.

Even though consistent with all our kinetic data, Scheme 3 is not without problems. There are two conditions that must be met for this mechanism to be realistic. The first is that protonation of **A** by water (k'_2), or the concerted process of step k'_{2c} , is much faster than expulsion of RO^- (k_2 in Scheme 2). If this is not the case, **A** would simply be converted to **C** (Scheme 2) instead of following the k'_2 or k'_{2c} path. The second is that, for the k'_2 step (or k'_{2c}) to be rate limiting, the relationship $k'_2 \ll k_{-1}$ (or $k'_{2c} \ll k_{-1}$) must hold. It is questionable whether both conditions can be met at the same time. The loss of OH^- from tetrahedral intermediates (**T**⁻) derived from carboxylic acid



esters is typically slower than the loss of RO^- ;¹² this is also the case for Meisenheimer complexes¹³ and the OH^- adduct of β -methoxy- α -nitrostilbene.¹⁴ If the same is true for **A** in Schemes 2 and 3, this would imply that $k_2 \gg k_{-1}$ (Scheme 2). Hence, if the condition for rate limiting protonation of **A**, $k'_2 \ll k_{-1}$, applies, the k'_2 step would be too slow to compete with the loss of RO^- from **A** (k_2 step in Scheme 2).

A third mechanism that is consistent with our kinetic data is shown in Scheme 4. There are two variations of this mechanism: one with a stepwise conversion of **1**⁻ into **F** via **E** (k''_2 and k''_3 ¹⁵), and the other with concerted protonation of the carbene carbon of **1**⁻ and carbene carbon–Cr bond cleavage (k''_{2c}). Assuming that the k''_2 step (or k''_{2c}) is rate limiting,

(12) (a) Bender, M. L.; Ginger, R. D.; Unik, J. P. *J. Am. Chem. Soc.* **1958**, *80*, 1044. (b) DeTar, D. *J. Am. Chem. Soc.* **1982**, *104*, 7205. (c) Marlier, J. F. *J. Am. Chem. Soc.* **1993**, *115*, 5953.

(13) Terrier, F. *Chem. Rev.* **1982**, *82*, 78.

(14) Bernasconi, C. F.; Fassberg, J.; Killion, R. B., Jr.; Schuck, D. F.; Rappoport, Z. *J. Am. Chem. Soc.* **1991**, *113*, 4937.

(15) Note that OH^- which is generated in the k''_2 step is only a spectator in the k''_3 step.

k_{obsd} for the first variation is given by eq 15, which simplifies to eq 16 for $\text{pH} \ll \text{p}K_{\text{a}}^{\text{CH}}$ and to eq 17 for $\text{pH} \gg \text{p}K_{\text{a}}^{\text{CH}}$,

$$k_{\text{obsd}} = \frac{\frac{K_{\text{a}}^{\text{CH}}}{K_{\text{w}}} k''_2 [\text{OH}^-]}{1 + \frac{K_{\text{a}}^{\text{CH}}}{K_{\text{w}}} [\text{OH}^-]} \quad (15)$$

$$k_{\text{obsd}} \frac{K_{\text{a}}^{\text{CH}}}{K_{\text{w}}} k''_2 [\text{OH}^-] \quad (16)$$

$$k_{\text{obsd}} = k''_2 \quad (17)$$

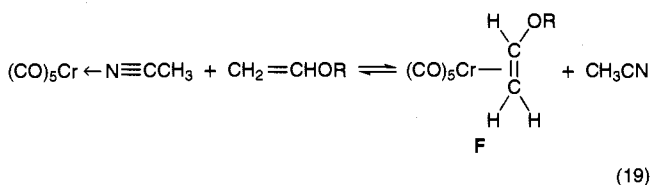
respectively. For the second variation the same equations are valid except that k''_2 is replaced by k''_{2c} .

Since both k''_2 and k''_{2c} involve proton transfer, the observed solvent kinetic isotope effect is consistent with the proposed mechanism. In the plateau region of the pH-rate profiles the $k_{\text{obsd}}(\text{H}_2\text{O})/k_{\text{obsd}}(\text{D}_2\text{O})$ ratio simply refers to $k''_2(\text{H}_2\text{O})/k''_2(\text{D}_2\text{O})$ or $k''_{2c}(\text{H}_2\text{O})/k''_{2c}(\text{D}_2\text{O})$, which is expected to reflect a substantial primary isotope effect, as observed. In the pH-dependent region $k_{\text{obsd}}(\text{H}_2\text{O})/k_{\text{obsd}}(\text{D}_2\text{O})$ is given by eq 18 (or a similar expression with $k''_2(\text{H}_2\text{O})$ and $k''_2(\text{D}_2\text{O})$)

$$\frac{k_{\text{obsd}}(\text{H}_2\text{O})}{k_{\text{obsd}}(\text{D}_2\text{O})} = \frac{K_{\text{a}}^{\text{CH}}(\text{H}_2\text{O}) K_{\text{w}}(\text{D}_2\text{O}) k''_2(\text{H}_2\text{O})}{K_{\text{a}}^{\text{CH}}(\text{D}_2\text{O}) K_{\text{w}}(\text{H}_2\text{O}) k''_2(\text{D}_2\text{O})} \quad (18)$$

which reflects the attenuation of the primary isotope effect by the factor $\{K_{\text{a}}^{\text{CH}}(\text{H}_2\text{O})/K_{\text{a}}^{\text{CH}}(\text{D}_2\text{O})\}\{K_{\text{w}}(\text{D}_2\text{O})/K_{\text{w}}(\text{H}_2\text{O})\}$ whose value is expected to be $< 1.1^1$

As mentioned in the Introduction, Fischer carbenes that are easily converted into their conjugate base by deprotonation of the carbon α to the carbene carbon typically lead to vinyl ethers (eq 2). Scheme 4 reflects this fact and also provides a mechanism for the conversion of the vinyl ether into acetaldehyde. This mechanism postulates that the initially formed vinyl ether be complexed with $\text{Cr}(\text{CO})_5$ (**F**)¹⁶ and that this complexation activates the vinyl ether toward hydrolysis¹⁷ in basic solution; without such complexation the vinyl ether is very stable toward basic hydrolysis (see Results). Our demonstration that acetaldehyde is formed in a basic solution of ethyl vinyl ether in the presence of $(\text{CO})_5\text{Cr}(\text{CH}_3\text{CN})$ supports our proposal because it suggests that the vinyl ether replaces the CH_3CN ligand of $(\text{CO})_5\text{Cr}(\text{CH}_3\text{CN})$, eq 19, to form **F** (Scheme 4).



On the basis of the above considerations, Scheme 4 appears to be the most attractive mechanism. A distinction between the stepwise and concerted conversion of **1**⁻ to **F** may be based

(16) Complexes of the type $(\text{CO})_5\text{Cr}(\text{olefin})$ are known, see, e.g.: (a) Wrighton, M.; Hammond, G. S.; Gray, H. B. *J. Organomet. Chem.* **1974**, *70*, 283. (b) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; p 953. (c) Klassen, J. K.; Selke, M.; Sorensen, A. A.; Yang, G. K. In *Bonding Energetics in Organometallic Compounds*; Marks, T. J., Ed.; American Chemical Society: Washington, DC, 1990; p 195.

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Table 2. Rate Constants for the Reactions of **1a**⁻ and **1b**⁻ with Water, Buffer Acids, and H_3O^+ in 50% CH_3CN -50% Water at 25 °C According to Scheme 4

proton donor ($\text{p}K_{\text{a}}^{\text{BH}}$)	symbol	1a ⁻ ($\text{p}K_{\text{a}}^{\text{CH}} = 12.50$)	1b ⁻ ($\text{p}K_{\text{a}}^{\text{CH}} = 12.97$)
H_2O (16.63)	k''_2 or k''_{2c} , s^{-1}	0.16	0.29
H_3BO_3 (10.66)	$k''_{2\text{BH}}$ or $k''_{2c\text{BH}}$, $\text{M}^{-1} \text{s}^{-1}$	≈ 0.021	
<i>N</i> -MeMorH ⁺ ^b (7.43)	$k''_{2\text{BH}}$ or $k''_{2c\text{BH}}$, $\text{M}^{-1} \text{s}^{-1}$	$\approx 4.1 \times 10^2$	
AcOH (5.93)	$k''_{2\text{BH}}$ or $k''_{2c\text{BH}}$, $\text{M}^{-1} \text{s}^{-1}$	$\approx 3.2 \times 10^4$	
H_3O^+ (-1.44)	$k''_{2\text{H}}$ or $k''_{2c\text{H}}$, $\text{M}^{-1} \text{s}^{-1}$	1.9×10^8	

^a $\mu = 0.1 \text{ M}$ (KCl). ^b *N*-Methylmorpholinium ion.

on the following considerations. The assumption that the stepwise reaction is the actual mechanism implies $k''_2 = 0.16 \text{ s}^{-1}$ for **1a** and 0.29 s^{-1} for **1b**. Based on these values one can estimate the acidity constant, $K_{\text{a}}^{\text{CrH}}$, of **E** from eq 20 ($\text{p}K_{\text{w}} =$

$$K_{\text{a}}^{\text{CrH}} = \frac{k''_{-2}}{k''_2} K_{\text{w}} \quad (20)$$

15.19).⁷ If one sets the highest possible value of k''_{-2} at $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for a diffusion controlled deprotonation,¹⁸ eq 20, applied to **1b**, gives

$$K_{\text{a}}^{\text{CrH}} = (2.23 \times 10^{-15}) k''_{-2} \leq 2.23 \times 10^{-5} \text{ M}$$

i.e., $\text{p}K_{\text{a}}^{\text{CrH}} \geq 4.65$. This lower limit compares with a $\text{p}K_{\text{a}}^{\text{CrH}}$ of 5.4 for $(\text{CO})_3\text{CpCrH}$ in 70% methanol-30% water¹⁹ (Cp = cyclopentadienyl), a compound that is likely to be more than one $\text{p}K_{\text{a}}$ unit less acidic than **E** because it has fewer electron withdrawing CO ligands than **E** and Cp is electron donating. These considerations suggest that the stepwise mechanism through **E** requires a $\text{p}K_{\text{a}}^{\text{CrH}}$ that is unrealistically high. Hence concerted conversion of **1**⁻ to **F** appears to be the preferred pathway.

Turning to the buffer catalyzed pathway, in the context of Scheme 4 k_{B} for general base catalysis takes on the meaning of $K_{\text{a}}^{\text{CH}} k''_{2\text{BH}}/K_{\text{a}}^{\text{BH}}$ or $K_{\text{a}}^{\text{CH}} k''_{2c\text{BH}}/K_{\text{a}}^{\text{BH}}$, respectively, with $k''_{2\text{BH}}$ referring to protonation of **1**⁻ on the metal by BH and $k''_{2c\text{BH}}$ to concerted conversion of **1**⁻ to **F** with BH as the proton donor. Even though it is likely that the reaction of **1**⁻ with buffer acids follows the same (concerted) mechanism as the reaction with water, the stepwise alternative cannot be discredited in a similar way as for the water reaction. The same is true of the reaction of **1**⁻ with H_3O^+ which is responsible for the plateau of the pH-rate profile below pH 9 (Figure 2); this plateau corresponds to $K_{\text{a}}^{\text{CH}} k''_{2\text{H}}$ or $K_{\text{a}}^{\text{CH}} k''_{2c\text{H}}$, respectively, where $k''_{2\text{H}}$ is the rate constant for protonation of **1**⁻ on the metal by H_3O^+ and $k''_{2c\text{H}}$ the rate constant for the H_3O^+ -promoted concerted conversion of **1**⁻ to **F**. The $k''_{2\text{BH}}$ (or $k''_{2c\text{BH}}$) values for the various buffers, along with k''_2 (or k''_{2c}) and $k''_{2\text{H}}$ (or $k''_{2c\text{H}}$) are summarized in Table 2.²⁰

Conclusions

The basic hydrolysis of **1a** and **1b** in 50% CH_3CN -50% water leads to acetaldehyde and the corresponding alcohol. There exist a number of plausible mechanisms for this reaction. They are shown in Schemes 2-4. All three schemes are consistent with the pH-rate profiles of Figures 2 and 3. Scheme 2, with

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(20) In view of the fact that the buffers used in this study do not belong to a common family, a Brønsted plot for $k''_{2\text{BH}}$ or $k''_{2c\text{BH}}$ would be meaningless and hence no such plot is shown.

either k_1 or k_2 as the rate limiting step, can be excluded because it is inconsistent with the kinetic solvent isotope effect data. Scheme 2 with k_3 as the rate limiting step can be rejected because the k_2 step cannot be considered truly reversible. A variation of Scheme 2 with k_4 or k_{4c} (eq 9) as the rate limiting step is consistent with the isotope effects but suffers from the same problems as the case where k_3 in Scheme 2 is rate limiting. Scheme 3 with either k'_2 or k'_{2c} as the rate limiting step is also consistent with the solvent isotope effect data, but the assumption that k'_2 or k'_{2c} is rate limiting is incompatible with the typical reactivity pattern of tetrahedral intermediates according to which RO^- is generally a better leaving group than OH^- . Scheme 4 with k'_{2c} as the rate limiting step is the only mechanism that is both consistent with the isotope effect data and does not violate well-known reactivity patterns. Scheme 4 with k''_2 as the rate limiting step is less attractive because it requires the $\text{p}K_{\text{a}}^{\text{CrH}}$ of **E** to be higher than expected based on the known $\text{p}K_{\text{a}}^{\text{CrH}}$ of $(\text{CO})_3\text{CpCrH}$.

Experimental Section

Materials. (Methoxy(methyl)carbene)pentacarbonylchromium(0) (**1a**) was prepared as described by Aumann and Fischer:²¹ yield 67%; mp 34.5–35.5 °C (lit.²¹ mp 34 °C); $^1\text{H NMR}$ (250 MHz, CDCl_3) δ 2.97 (s, 3H, CH_3) and 4.72 (s, 3H, OCH_3); UV (50% CH_3CN –50% H_2O) λ_{max} 372 nm, $\log \epsilon = 3.81$. (Ethoxy(methyl)carbene)pentacarbonylchromium(0) (**1b**) was synthesized according to the procedure described by Fischer and Fischer:²² yield 40%, oil; $^1\text{H NMR}$ (250 MHz, CD_3CN) δ 1.00 (t, 3H, CH_3), 3.34 (q, 2H, CH_2), 4.74 (s, 3H, OCH_3); UV (50% CH_3CN –50% H_2O) λ_{max} 370 nm, $\log \epsilon = 3.78$. $\text{Cr}(\text{CO})_6$ (Aldrich, 99%) was used without further purification. *N*-Methylmorpholine was refluxed over NaOH and freshly distilled prior to use. Acetic acid and borate were used as received. KOH and HCl solutions were prepared using "dilut-it" from Baker Analytical. Acetonitrile was refluxed over CaH_2 and distilled under argon. Water was taken from a Milli-Q water purification system. D_2O (Aldrich, 99.9% atom % D) was used as received.

Product Studies. A. Hydrolysis of 1a. The reaction mixture, 50–100 mg of **1a** and 0.01 M KOH in 1–2 mL of 50% CH_3CN –50% water, was stirred overnight at 45–50 °C. After extraction with CDCl_3 and drying over Na_2SO_4 the products were analyzed by $^1\text{H NMR}$. Quantitation of the acetaldehyde yield was accomplished by adding THF as internal standard and using a mixture of acetaldehyde and THF of known composition as a reference. The analysis showed that $\geq 90\%$ of **1a** had been converted to acetaldehyde; no starting material could be detected in the product solution. In a slight modification of the procedure, the reaction was carried out in one arm of a tube shaped like an inverted U. The other arm contained CDCl_3 cooled with a dry ice–ethanol mixture (–72 °C) and acted as a trap for the volatile hydrolysis products acetaldehyde and methanol. $^1\text{H NMR}$ analysis of the CDCl_3 solution again showed an acetaldehyde yield of $\geq 90\%$.

B. Hydrolysis of 1b. **1b** (230 mg) in 5 mL of acetonitrile was mixed with 5 mL of 0.2 M KOH in water at ambient temperature and stirred for 2 h. The solution turned green and some white precipitate formed. CDCl_3 (3 mL) and 1 mL of saturated KCl were added. After vigorous shaking the mixture was subjected to evaporation under reduced pressure and the volatile fractions (CDCl_3 , EtOH, and CH_3CHO) were trapped in a vessel cooled by dry ice–ethanol. After being dried over Na_2SO_4 the distillate was analyzed by $^1\text{H NMR}$: acetaldehyde and ethanol were the only detectable compounds.

C. Hydrolysis of Ethyl Vinyl Ether in the Presence of $\text{Cr}(\text{CO})_5$ – (CH_3CN) . $(\text{CO})_5\text{Cr}(\text{CH}_3\text{CN})$ was generated in situ by irradiating $\text{Cr}(\text{CO})_6$ in acetonitrile.²³ In a typical experiment, 0.14 g (0.65 mmol) of $\text{Cr}(\text{CO})_6$ in 15 mL of acetonitrile was irradiated for 2 h with a UVSL-25 Mineralight lamp (254/366 nm); the formation of $(\text{CO})_5\text{Cr}(\text{CH}_3\text{CN})$ was monitored by UV spectroscopy. After the irradiation was discontinued, 0.30 g (4.2 mmol) of ethyl vinyl ether and 5 mL of 0.02 M KOH were added to the solution. Some white precipitate formed immediately. The suspension was stirred for 15 h at room temperature. The procedure was carried out under argon in the same tube shaped like an inverted U described in the section Hydrolysis of **1a**, and the products were again trapped by cold CDCl_3 placed into the other arm of the tube. Acetaldehyde and unreacted ethyl vinyl ether were identified by $^1\text{H NMR}$. An approximate 40% yield of acetaldehyde was calculated based on the amount of aldehyde detected in the CDCl_3 solution used as a trap and a calibration of this trapping method with known mixtures of acetaldehyde and ethyl vinyl ether.

Kinetic Runs and Spectra. In KOH solution the rates were measured in an Applied Photophysics DX.17MV stopped-flow apparatus, and in the borate, *N*-methylmorpholine, and acetate buffers as well as in the HCl solutions the rates were determined in a Perkin Elmer Lambda 2 UV/vis spectrophotometer. At $\text{pH} < \text{p}K_{\text{a}}^{\text{CH}}$ where the reaction corresponds to conversion of **1** to products, the kinetics were monitored at 372 (**1a**) and 370 nm (**1b**), respectively; at $\text{pH} > \text{p}K_{\text{a}}^{\text{CH}}$ where the reaction corresponds to conversion of **1**[–] to products, the measurements were performed at 270 (**1a**) and 280 nm (**1b**), respectively. Reaction solutions were always freshly prepared just prior to the experiment by injecting a small amount of stock solution of the carbene complex in acetonitrile into the 50% acetonitrile–50% water medium.

Spectra (Figure 1) were taken in a Hewlett Packard HP8452A diode array spectrophotometer.

pH and $\text{p}K_{\text{a}}$ Measurements. The pH in 50% acetonitrile–50% water was determined according to eq 21²⁴ with pH_{meas} referring to the reading of the pH-meter calibrated with standard aqueous buffers. The

$$\text{pH} = \text{pH}_{\text{meas}} + 0.18 \quad (21)$$

$\text{p}K_{\text{a}}^{\text{BH}}$ values of H_3BO_3 , acetic acid, and *N*-methylmorpholinium ion were determined by measuring the pH of buffer solutions prepared in a 1:1 ratio. The pH of reaction solutions for stopped-flow runs was measured in mock mixing experiments that simulated the stopped-flow runs.

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