

Table I. Absolute and "Apparent" Rate Constants for the Reaction of Adamantanylidene with Various Quenchers, in Benzene at Ambient Temperature

quencher	precursor concn, M	k , M ⁻¹ s ⁻¹ (direct meth, carbene 2) ^a	$k_q\tau$ (τ , μ s) (Stern-Volmer meth, carbene 2 and excited state 1*) ^b	"apparent" k , M ⁻¹ s ⁻¹ (Stern-Volmer meth, carbene 2) ^b	concn range of quencher, M
thiophene		$1.75 \pm 0.6 \times 10^6$	—	—	0.12–0.312
diazirine 1		$2.87 \pm 0.41 \times 10^7$	—	—	(7.23×10^{-4}) – (1.27×10^{-2})
pyridine	2.32×10^{-4}	$1.54 \pm 0.23 \times 10^6$	4.25 ^c (2.30)	$1.85 \pm 0.84 \times 10^6$	0–0.371
<i>n</i> -butyl vinyl ether	3.23×10^{-4}	$3.80 \pm 0.27 \times 10^5$	0.54 ^c (1.14)	$4.73 \pm 0.27 \times 10^5$	0–1.55
diethyl fumarate	2.99×10^{-4}	$1.53 \pm 0.24 \times 10^6$	11.18 ^d (1.91)	$5.85 \pm 0.34 \times 10^6$	0–0.214
triethylsilane	3.16×10^{-4}	$3.31 \pm 0.42 \times 10^5$	1.73 ^d (2.65)	$6.52 \pm 0.66 \times 10^6$	0–1.41
diphenylsilane	2.99×10^{-4}	$1.02 \pm 0.10 \times 10^6$	14.81 ^d (1.98)	$7.49 \pm 0.65 \times 10^6$	0–0.14
phenylsilane	2.99×10^{-4}	$2.03 \pm 0.30 \times 10^6$	25.17 ^d (1.95)	$1.3 \pm 0.1 \times 10^7$	0–0.162
<i>p</i> -nitrophenol ^f	1.04×10^{-2}	$3.41 \pm 0.76 \times 10^9$	—	—	(1.37×10^{-4}) – (2.4×10^{-3})
acetic acid	1.85×10^{-4}	$5.55 \pm 0.48 \times 10^9$	6934 ^e (2.03)	$3.41 \pm 0.25 \times 10^9$	0–0.0042
acetic acid- <i>d</i>	1.50×10^{-4}	$4.81 \pm 0.65 \times 10^9$	5400 ^e (3.40)	$1.59 \pm 0.12 \times 10^9$	0–0.012
methanol	2.42×10^{-4}	<i>g</i>	85 ^e (2.10)	—	0–0.05
methanol- <i>d</i> ₄	1.86×10^{-4}	<i>g</i>	33 ^e (1.97)	—	0–0.11
2-propanol	1.83×10^{-4}	<i>g</i>	27 ^e (2.35)	—	0–0.20
<i>tert</i> -butyl alcohol	1.39×10^{-4}	<i>g</i>	13 ^e (2.50)	—	0–0.36

^a Absolute rate constants of reaction of adamantanylidene 2 obtained by measuring the effect of quencher on the rate constant of formation of thiophene ylide 3a. ^b Apparent $k_q\tau$ values obtained from the effect of the quencher on the yield of thiophene ylide 3; the variation in τ is due to variation in [1]. ^c Quencher intercepts mainly carbene 2. ^d Quencher intercepts both carbene 2 and transient precursor. ^e Quencher intercepts only the transient precursor of the carbene. ^f Absolute rate constant of 2 with *p*-nitrophenol obtained by monitoring the growth rate of *p*-nitrophenolate ion. ^g Too slow to measure. ^h These numbers were calculated for the sake of comparison only using τ values of carbene 2. The apparent rate constants are meaningful for adamantanylidene only for pyridine, acetic acid, acetic acid-*d*, and *n*-butyl vinyl ether.

of 4 has been observed by Moss^{4a} and found to be persistent at –78 °C. It is economical to hypothesize that the transient precursor to carbene 2 may also isomerize to diazo compound 4 as shown in Scheme I, but our data do not require this to be the case. We suspect that much chemistry that could be reasonably attributed to carbene 2 may actually derive from reactions of the transient precursor to carbene 2 and to the ground state of 4. In fact the immediate photochemical production of 2 may well be a minor process as the analogous yield of ylide 3b is 3 times lower than the yield of ylide derived from the reaction of another dialkylcarbene, homocubanylidene,^{5f} with pyridine, as determined by LFP.¹² Photoisomerization of 1 may well be the major process as photolysis of 1 at 96 K in 3-methylpentane produces an intense IR band at 2042 cm⁻¹ which is most reasonably attributed to 4.

Our inability to measure the rate constant of reaction of 2 with methanol does not mean that the carbene does not react with this alcohol. It means only that the concentrations of methanol needed to intercept 2 are sufficient to intercept the transient carbene precursor (1*, 2*, or 4*) and thereby prevent the formation of the carbene. The rate constant of reaction of acetic acid with 2 is very large. Thus the measurement of the absolute rate constant of reaction of 2 with acetic acid required the presence of only a small quantity of quencher. The acetic acid was sufficiently dilute that the transient carbene precursor was not intercepted and the kinetics of 2 could be discerned by the effect of quencher on both the rate of formation and the yield of ylide 3a.

The recent report of Kirmse¹³ and co-workers on the protonation of diphenylcarbene prompted us to attempt a similar reaction with adamantanylidene. LFP of 1 in the presence of highly dilute *p*-nitrophenol in acetonitrile produces the *p*-nitrophenoxide ion. A plot of the absolute rate constant of phenolate ion formation versus *p*-nitrophenol concentration is linear, and the slope of this plot is equal to the rate constant of reaction of 2 with *p*-nitrophenol (Table I).⁹ The inverse of the intercept of this plot ($\tau = 965$ ns) is comparable to that observed in the thiophene quenching plot, which suggests that it is carbene 2 rather than 1*, 2*, or 4* that is reacting with dilute *p*-nitrophenol to form ion pair 6. It is clear that the reaction of 2 with hydroxylic substrates proceeds by proton transfer, which explains why the more acidic quenchers (acetic acid, *p*-nitrophenol) are so much more effective at interception of adamantanylidene than simple alcohols.

It is interesting to note that adamantanylidene 2 reacts much more slowly with typical scavengers such as methanol and pyridine than does the only other dialkylcarbene, homocubanylidene,^{5f} studied as yet by LFP techniques. The study of pyridine and *p*-nitrophenol trapping of other dialkylcarbenes is in progress to discover the origin of this effect.

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Supplementary Material Available: Transient spectra of ylides 3a and 3b and of *p*-nitrophenolate ion and a plot of the observed rate constant of formation of *p*-nitrophenolate ion as a function of *p*-nitrophenol concentration (4 pages). Ordering information is given on any current masthead page.

CO Is neither an Intermediate nor a Catalyst in MTG Chemistry on Zeolite HZSM-5

Eric J. Munson, Noel D. Lazo, Meg E. Moellenhoff, and James F. Haw*

Department of Chemistry, Texas A&M University
College Station, Texas 77843

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Two conflicting roles for CO in the conversion of methanol to gasoline on zeolite HZSM-5 (MTG process¹) have recently been proposed. In their studies of the reaction of methanol on HZSM-5, Anderson and Klinowski,² observing the presence of CO prior to hydrocarbon formation and its absence afterward, concluded that CO is an intermediate in the reaction. This was rationalized by proposing that CO and methanol undergo Fisher-Tropsch style chemistry on Fe³⁺ impurities to form ethanol, which then eliminates ethylene. In another recent paper, Jackson and Bertsch³

* To whom correspondence should be addressed.

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(2) Anderson, M. W.; Klinowski, J. *J. Am. Chem. Soc.* 1990, 112, 10.

(12) This assumes that the extinction coefficients of 3b and the homocubanylidene-pyridine ylide are comparable.

(13) Kirmse, N.; Kilian, J.; Steenken, S. *J. Am. Chem. Soc.* 1990, 112, 6399.

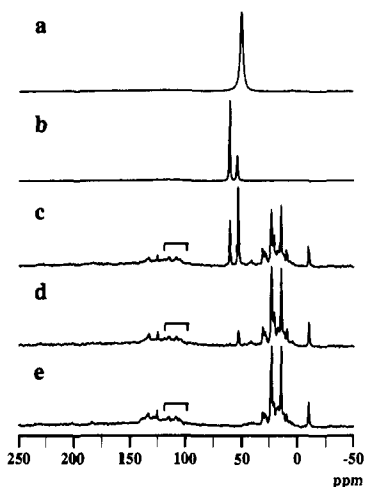


Figure 1. In situ ^{13}C MAS NMR spectra showing the conversion of methanol- ^{13}C to hydrocarbons on zeolite catalyst HZSM-5: (a) at 298 K prior to raising the probe temperature; (b) after 5 min at 523 K; (c) after 150 min at 523 K; (d) after 180 min at 523 K; (e) after 210 min at 523 K. Background signals from Kel-F endcaps, which were used to seal the sample rotor, are denoted by brackets.

studied the conversion of methanol to hydrocarbons in polyphosphoric acid solution (Pearson reaction). They proposed that after CO forms during an induction period, it catalyzes methanol conversion to either ethylene or propene. Drawing on the work of Anderson and Klinowski,² Jackson and Bertsch further proposed that CO should exert an identical catalytic role in HZSM-5. In this communication, we report in situ ^{13}C solid-state MAS NMR experiments that demonstrate that CO is neither an intermediate nor a catalyst in the conversion of methanol to gasoline on HZSM-5.

In the standard protocol for our experiments, methanol- ^{13}C was adsorbed onto the catalyst³ and the sample was heated rapidly (1 °C/s) from 298 K to 523 K in the magic-angle spinning (MAS) probe. Three consecutive experiments gave essentially identical time courses and product distributions; hydrocarbon formation began after 90 ± 20 min at 523 K, and 30% conversion was achieved after 120 ± 20 min. Figure 1 shows ^{13}C MAS NMR spectra from a representative experiment. Figure 1a is the spectrum of methanol- ^{13}C (51 ppm) on HZSM-5 at 298 K prior to heating. Immediately after equilibration of the NMR probe temperature to 523 K, the methanol was partially condensed to dimethyl ether (62 ppm, Figure 1b). After 150 min at 523 K, resonances from -10 to 50 ppm showed the formation of hydrocarbons (Figure 1c). Figures 1d,e show ^{13}C spectra that tracked the progressive conversion of methanol and dimethyl ether to hydrocarbons. Reproducible reaction rates and product distributions were obtained with the above protocol when careful attention was given to catalyst activation conditions,¹ probe temperature, and sample loading.

(3) Jackson, J. E.; Bertsch, F. M. *J. Am. Chem. Soc.* **1990**, *112*, 9085.

(4) (a) White, J. L.; Lazo, N. D.; Richardson, B. R.; Haw, J. F. *J. Catal.* **1990**, *125*, 260. (b) Lazo, N. D.; White, J. L.; Munson, E. J.; Lambregts, M.; Haw, J. F. *J. Am. Chem. Soc.* **1990**, *112*, 4050.

(5) Zeolite $\text{NH}_4\text{ZSM-5}$ (obtained from UOP Corporation, Si/Al = 38, Fe content = 800 ppm) was activated by a multistep procedure, transferred to a zirconia rotor, and loaded into the CAVERN apparatus prior to adsorption (see: Haw, J. F.; Richardson, B. R.; Oshiro, I. S.; Lazo, N. D.; Speed, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 2052). Methanol- ^{13}C (99% ^{13}C) and formic acid- ^{13}C (99% ^{13}C) were obtained from Cambridge Isotopes and purified via several freeze-pump-thaw cycles. Depending on the experiment, 2.4 mmol/(g of catalyst) of methanol or 2.4 and 0.6 mmol/(g of catalyst) of methanol and formic acid, respectively, were adsorbed onto the catalyst via standard vacuum-line techniques. In experiments with formic acid, the formic acid was always adsorbed onto the catalyst first. The rotor was subsequently sealed (see: Haw, J. F.; Speed, J. A. *J. Magn. Reson.* **1988**, *78*, 344) and immediately transferred to the spectrometer. ^{13}C NMR spectra were obtained on a Chemagnetics CMX-300 NMR spectrometer using single-pulse excitation with proton decoupling (pulse delay = 2 s, 100 transients) and magic-angle spinning (MAS).

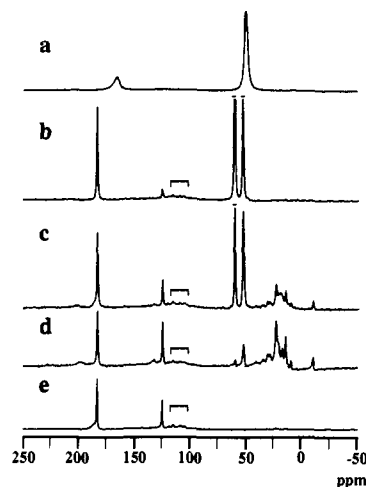


Figure 2. In situ ^{13}C MAS NMR spectra showing the chemistry of formic acid- ^{13}C and methanol- ^{13}C (a-d) and of formic acid- ^{13}C and unlabeled methanol (e) on HZSM-5: (a) at 298 K prior to raising the probe temperature; (b) after 5 min at 523 K, showing conversion of formic acid to CO; (c) after 150 min at 523 K; (d) after 210 min at 523 K; (e) same as d except that unlabeled methanol was used, demonstrating that the label from ^{13}CO is not incorporated into the hydrocarbon products. Background signals from Kel-F endcaps, which were used to seal the sample rotor, are denoted by brackets.

If CO catalyzes the reaction of methanol to hydrocarbons on HZSM-5, large quantities of added CO should obviously increase the reaction rate. To test this hypothesis, methanol- ^{13}C and formic acid- ^{13}C were coadsorbed onto the catalyst⁵ and an in situ NMR experiment was performed with the above protocol. Formic acid was used to generate CO in situ,⁶ as CO does not adsorb directly in significant quantities at modest pressures. Figure 2a shows the ^{13}C MAS NMR spectrum prior to heating, with peaks at 165 and 51 ppm corresponding to formic acid and methanol, respectively. The conversion of formic acid to CO (184 ppm) is evident in Figure 2b, which was obtained immediately after reaching a temperature of 523 K. After 150 min (Figure 2c), CO had been partially converted to CO_2 (126 ppm) via the water-gas shift reaction and the conversion to hydrocarbons had begun. After 210 min at 523 K, the conversion to hydrocarbons was almost complete (Figure 2d). Comparing Figures 1 and 2a-d, the only apparent difference is the presence of CO and its conversion to CO_2 via the shift reaction. We conclude that the conversion rate is not obviously increased by the presence of large quantities of CO.

In order to establish whether or not CO is an intermediate in the conversion of methanol on HZSM-5, the experiment shown in Figures 2a-d was repeated, except that unlabeled methanol was used; the ^{13}C MAS NMR spectrum taken after 210 min at 523 K is shown in Figure 2e. If CO were an intermediate in this reaction, a significant amount of the ^{13}C label should have been incorporated into the hydrocarbon products. As is evident from Figure 2e, no such label incorporation occurred. Furthermore, in a number of in situ experiments in which small amounts of CO were observed to form naturally, we could always quantitatively account for its subsequent consumption by the formation of CO_2 (spectra not shown).

The above results demonstrate that CO is neither an intermediate nor a catalyst in the conversion of methanol to hydrocarbons on HZSM-5, in contradiction to proposals in two recent papers in this journal.

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