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Kinetics of Hydrogen Atom Transfer from $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$ to Various Olefins: Influence of Olefin Structure

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Abstract: Treating $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$ (**1**) or $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{D}$ (**1-d₁**) with an excess of olefin containing the opposite isotope generally leads to H/D exchange, although hydrogenation is also observed in some cases. Application of an appropriate statistical correction to the observed exchange rate gives k_{H} and k_{D} , the rate constants for H• (D•) transfer from $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$ (D) to various olefins. The values of k_{H} and k_{D} vary appreciably with the substituents on the double bond. Phenyl-substituted olefins accept H• more readily than do carbomethoxy-substituted olefins, although the latter accept H• more readily than do alkyl-substituted olefins. A methyl substituent on the incipient radical site increases k_{H} at 323 K by a factor between 5 and 50. A methyl substituent on the carbon to which the H• is being transferred decreases k_{H} substantially. On the whole, the rate constants for H• transfer reflect steric effects as well as the stability of the resulting carbon-centered radicals.

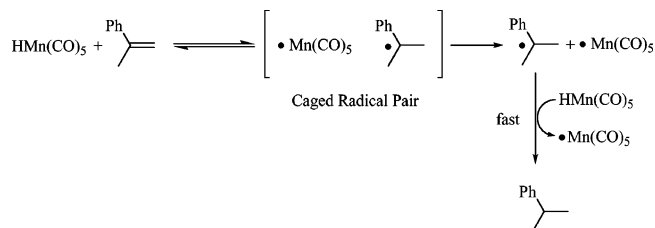
Introduction

Hydrogen atom (H•) transfers from transition-metal hydrides to organic molecules play an important role in many reactions.^{1,2} For example, H• transfer from transition-metal hydrides is involved in some hydrogenations. In 1977, Sweany and Halpern³ reported strong evidence for H• transfer in the hydrogenation of α -methylstyrene by $\text{HMn}(\text{CO})_5$ (Scheme 1); they observed chemically induced dynamic nuclear polarization (CIDNP) and an inverse isotope effect for $\text{HMn}(\text{CO})_5/\text{DMn}(\text{CO})_5$. Since then, there have been numerous reports of hydrogenations that occur through H• transfer.^{2,4}

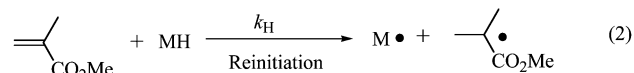
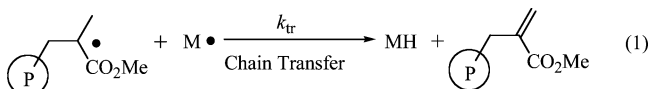
In such a hydrogenation the first H• transfer, from the transition-metal hydride to an unsaturated carbon–carbon bond, generates a metalloradical and a carbon-centered radical. A second H• transfer, from a second equivalent of the hydride to the intermediate carbon-centered radical, produces the hydrogenated product.

Hydroformylation reactions may also involve H• transfer. Evidence for such a step in the hydroformylation of styrene by $\text{HCo}(\text{CO})_4$ is offered by an inverse H/D kinetic isotope effect ($k(\text{HCo}(\text{CO})_4)/k(\text{DCo}(\text{CO})_4)$) and by the absence of an inverse CO dependence in the rate law.^{1,4c}

Scheme 1



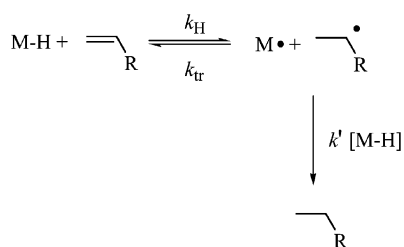
An H• transfer from a transition-metal hydride to a carbon–carbon double bond also occurs in catalysis of chain transfer by metalloradicals during free radical polymerizations.^{5,6} In eq 1, H• abstraction from a propagating radical by the chain-transfer catalyst $\text{M}^•$ generates a vinyl-terminated polymer and a metal hydride complex. In eq 2, H• transfer from the hydride complex to monomeric olefin reinitiates the chain. While direct observation of eq 2 with Co(II) and Mo(III) chain-transfer catalysts has been hampered by the instability of the corresponding hydride complexes, we have observed eq 2 directly, initiating the polymerization of MMA with $(\eta^5\text{-C}_5\text{Ph}_5)\text{Cr}(\text{CO})_3\text{H}$.⁶



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- (6) Abramo, G. P.; Norton, J. R. *Macromolecules* **2000**, *33*, 2790–2792.

Scheme 2



Despite the importance of metal-to-olefin H• transfer, few kinetic studies^{4b,7,8} have been reported. If the rate-determining step in a hydrogenation is the first H• transfer to the olefin, and the resulting organic radical receives the second H• (rate constant $k'[\text{M-H}]$) faster than it transfers the first H• back to M• (rate constant $k_{\text{tr}}[\text{M}^\bullet]$) (see Scheme 2), it is simple to determine k_{H} from the rate at which M-H disappears in the presence of excess olefin. However, the kinetics become more complicated when back transfer ($k_{\text{tr}}[\text{M}^\bullet]$) competes with the second H• transfer ($k'[\text{M-H}]$); k_{H} cannot then be deduced from the overall rate of the reaction. Bullock and Samsel have shown how kinetic simulations can be used to obtain k_{H} in a case—the reaction between α -cyclopropylstyrene and (η^5 -C₅H₅)Cr(CO)₃H—where back transfer is significant.⁷

Three years ago we obtained rate constants for H• transfer from (η^5 -C₅R₅)Cr(CO)₃H (R = Ph, Me, H) to styrene-*d*₈ and methyl methacrylate-*d*₅ (MMA-*d*₅) by monitoring H/D exchange.⁹ We found that k_{H} for MMA decreased as the chromium hydride became more congested, while k_{H} for styrene was less affected by the steric bulk of the hydride.

In the present paper, we report rate constants for H•/D• transfer from (η^5 -C₅H₅)Cr(CO)₃H (**1**) or (η^5 -C₅H₅)Cr(CO)₃D (**1-d**₁) to variously substituted olefins: 1,1-diphenylpropene (**2**), 1,1-diphenylethylene (**3**), α -methylstyrene (**4**), methyl crotonate (**5**), 1-octene (**6**), (*E*)-2-methylbut-2-enoic acid methyl ester (methyl tiglate, **7**), and 2-methyl-1-heptene (**8**) (Figure 1). Such transfers lead to H/D exchange or hydrogenation or both, depending on the olefin substituent. The k_{H} values thereby obtained should be useful in predicting synthetic applications of H• transfer chemistry.

Results

H/D Exchange between (η^5 -C₅H₅)Cr(CO)₃D (1-d**₁) and 1,1-Diphenylpropene (**2**).** When a solution of **1-d**₁ was treated with a large excess of **2** in C₆D₆ at 323 K, an exponential increase in the hydride resonance of **1** was observed (Figure 2) in the ¹H NMR. ²H NMR confirmed that H/D exchange had occurred (eq 3), as a signal from the vinyl deuterium of **2-d**₁ appeared while that from the deuteride resonance of **1-d**₁ decreased. Only a trace of the hydrogenation product, 1,1-diphenylpropane, was observed after an hour or two of reaction.

Monitoring the increase of the hydride ¹H NMR resonance under these conditions (excess **2**) gave a pseudo-first-order rate constant, k_{obs} (eq 4). Varying [**2**] from 0.29 to 1.0 M (Table

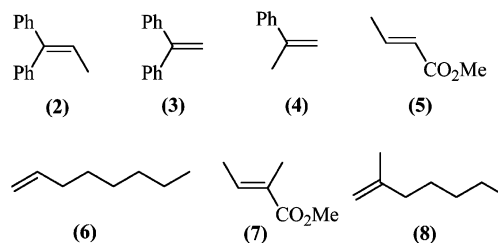


Figure 1. Olefins studied as H• transfer acceptors.

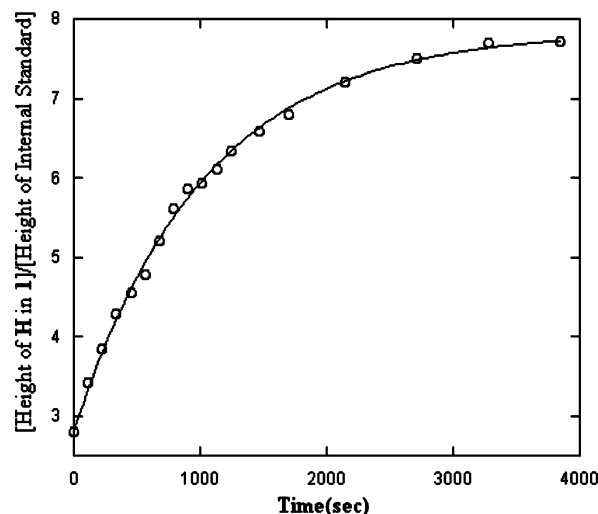
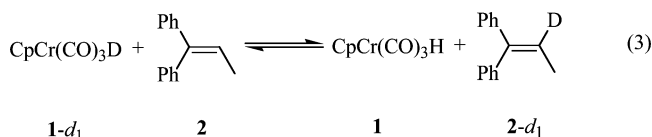


Figure 2. Growth of **1** from H/D exchange between **2** (1.0 M) and **1-d**₁ (0.03 M) at 323 K in C₆D₆. The curve is calculated with the best-fit k_{obs} and [**1**]_∞.



$$-\frac{d[\text{Cr-D}]}{dt} = k_1[\text{2}][\text{Cr-D}] = k_{\text{obs}}[\text{Cr-D}] \quad (4)$$

S1) showed that k_{obs} was a linear function of [**2**] (Figure 3), confirming that exchange was first-order in each reactant, second-order overall, as shown in eq 4. The slope of Figure 3 showed that k_1 was $9.8(4) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ at 323 K.

Extracting k_{D} , the rate constant for the first D• transfer in Scheme 3, from k_1 requires knowledge of the fractional probability S (eq 5) that H• will return to the chromium radical after the initial transfer. If we define k_{trH} and k_{trD} as the second-order rate constants for H• transfer and D• transfer, respectively, from the radical **9-d**₁ to Cr• (= CpCr(CO)₃•), we can write the fractional probability S as in eq 6. The isotope effect $k_{\text{trH}}/k_{\text{trD}}$ can be estimated, as in our previous paper, by comparing the rate constant for termination during an MMA-*d*₀ polymerization with that during an MMA-*d*₅ polymerization;¹⁰ the ratio, a C→C isotope effect for the transfer of H•/D• from an MMA chain-carrying radical, is 2.93 at 60 °C. Our C→Cr isotope effect can also be estimated from the ratio of the efficiency of a cobalt catalyst for chain transfer during the polymerization of MMA to the efficiency of the same catalyst during the polymerization of MMA-*d*₈; this ratio has an average value of 3.5 between 40

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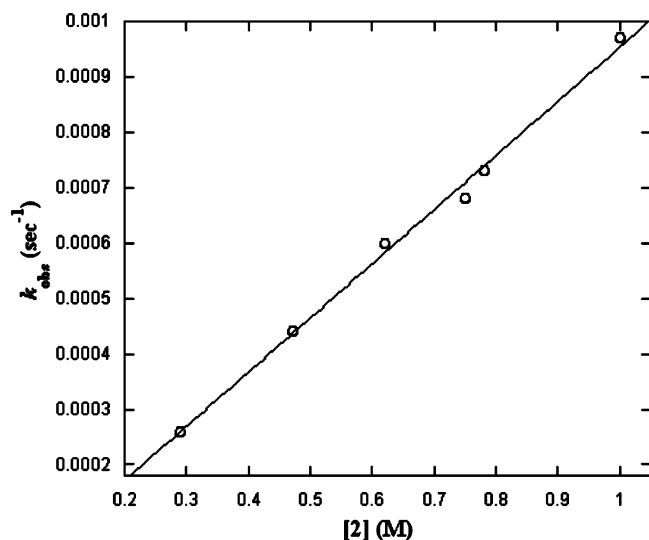
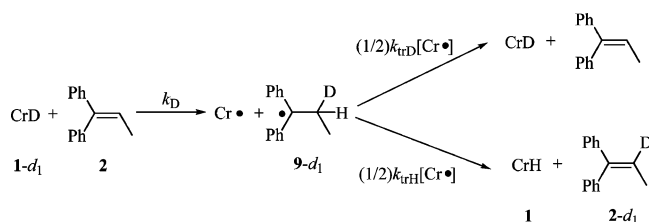


Figure 3. Plot of k_{obs} vs $[2]$ for D^* transfer from 1-d_1 to 2 at 323 K in C_6D_6 .

Scheme 3



and 80 °C.¹¹ Our H^*/D^* transfer from carbon to chromium is downhill by 12 kcal/mol,⁹ which argues for an early transition state and against the large isotope effect associated with a thermoneutral transfer and a symmetric transition state.⁸ The only reason to think our isotope effect might be large is a recent investigation by Bullock and co-workers of the reaction between 1,4-cyclohexadiene and $\text{CpOs}(\text{CO})_2^*$; indirect observations are consistent with an isotope effect between 4 and 20.¹² The Bullock reaction is, however, more nearly thermoneutral than ours.

$$k_1 = S k_D \quad (5)$$

$$S = \frac{1/2 k_{\text{tH}}[\text{Cr}^*]}{1/2 k_{\text{tD}}[\text{Cr}^*] + 1/2 k_{\text{tH}}[\text{Cr}^*]} = \frac{k_{\text{tH}}/k_{\text{tD}}}{1 + k_{\text{tH}}/k_{\text{tD}}} \approx \frac{3}{4} \quad (6)$$

If we estimate the kinetic isotope effect, $k_{\text{tH}}/k_{\text{tD}}$, as 3 as in our previous paper,^{9,13} S will be 0.75 (eq 6). The value of S is not very sensitive to the kinetic isotope effect; a 10% variation in $k_{\text{tH}}/k_{\text{tD}}$ would change S only by 3%. Dividing k_1 by S gives a k_D of $1.31(5) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for 2 at 323 K.

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(13) We have used the same estimate (3) of $k_{\text{tH}}/k_{\text{tD}}$ for all transfers of H^*/D^* from carbon-centered radicals back to Cr^* because the radicals in question are similar (tertiary) and none of the equations for S is very sensitive to this isotope effect (see text).

Scheme 4

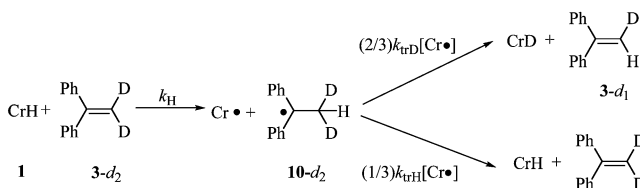


Table 1. Values of k_H and Activation Parameters for Isotope Exchange between 1 and 3-d_2 in Toluene- d_8

T (K)	$k_H (\times 10^{-2} \text{ M}^{-1} \text{ s}^{-1})$	ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (eu)
263.7	0.544(7)		
270.2	1.01(2) ^a		
278.2	2.03(8)	12.0(5)	−23(2)
283.7	2.90(5)		
323.0	46(6) ^b		

^a Data plotted in Figure S1. ^b Extrapolation from activation parameters.

Reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$ (1) with 1,1-Diphenyl-ethylene-2,2- d_2 (3-d_2) and α -Methylstyrene- d_5 (4-d_5). H/D exchange between 1 and an excess of 3-d_2 or 4-d_5 proved too rapid to follow by ^1H NMR at 323 K. However, kinetic experiments at lower temperatures were straightforward. Treatment of 1 with an excess of 3-d_2 in toluene- d_8 at 270 K and examination of the resulting solution by ^1H NMR showed an exponential decay in the hydride resonance of 1 (Figure S1), along with a smooth increase in the resonance (δ 5.41) of the 3-d_1 arising from the H/D exchange in Scheme 4. No hydrogenated product was observed.

Monitoring the decay of the hydride resonance under these conditions (excess 3-d_2) gave a pseudo-first-order rate constant, k_{obs} , as defined in eq 7. We can assume that H^* transfers to other substrates also obey second-order rate laws like that (eq 4) established for 2 ; such rate laws have been reported for the transfer of H^* from many hydrides to many olefins.⁸ Thus, we can obtain values of k_2 and k_H , the rate constant for the first H^* transfer in Scheme 4, at various temperatures from expressions (eqs 8 and 9) similar to those used with 2 . The fractional probability S (eq 8) that D^* will return to the chromium radical after the initial transfer can be estimated as 0.4 from eq 9. In this case, S is more sensitive to the kinetic isotope effect; a 10% variation in $k_{\text{tH}}/k_{\text{tD}}$ would change S and k_H by 6%. The values of k_H at each temperature and the activation parameters are given in Table 1.

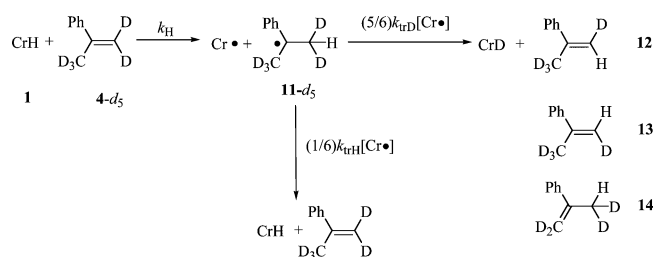
$$-\frac{d[\text{Cr-H}]}{dt} = k_2[3\text{-d}_2][\text{Cr-H}] = k_{\text{obs}}[\text{Cr-H}] \quad (7)$$

$$k_2 = S k_H \quad (8)$$

$$S = \frac{2/3 k_{\text{tD}}[\text{Cr}^*]}{2/3 k_{\text{tD}}[\text{Cr}^*] + 1/3 k_{\text{tH}}[\text{Cr}^*]} = \frac{2}{2 + k_{\text{tH}}/k_{\text{tD}}} \approx \frac{2}{5} \quad (9)$$

Similarly, 1 was treated with an excess of 4-d_5 in C_6D_6 at temperatures from 283 to 306 K. A similar exponential decay of the hydride resonance of 1 was observed, along with growth of three proton resonances corresponding to the isotopomers

Scheme 5

**Table 2.** Values of k_H and Activation Parameters for Isotope Exchange between **1** and **4-d₅** in C₆D₆

T (K)	$k_H (\times 10^{-2} \text{ M}^{-1} \text{ s}^{-1})$	ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (eu)
283.2	0.31(1)		
289.6	0.56(2)		
295.6	0.97(2) ^a		
301.1	1.47(2)	14.1(2)	-20.1(7)
306.2	2.2(1)		
323.0	7.9(3) ^b		

^a Data plotted in Figure S2. ^b Extrapolation from activation parameters

12 (δ 5.02), **13** (δ 5.38), and **14** (δ 1.98) (Scheme 5). The ratio of the **12**, **13**, and **14** resonances was 1:1:3, reflecting the expected equal probability of introducing H into each of the two vinyl positions and the expected relative probability, 2:3, of abstracting D• from the CHD₂ vs the CD₃ of the intermediate radical **11-d₅**. We also observed a little of the hydrogenation product cumene, in amounts implying that between 2 and 10% of the hydride **1** had been consumed by this side reaction.

For simplicity, we ignored the hydrogenation and calculated an observed pseudo-first-order rate constant, k_{obs} , at various temperatures from the decline in the hydride resonance of **1**. We then obtained values of k_H , the rate constant for the first H• transfer in Scheme 5, from an expression (eq 10) for S , the fractional probability that D• will return to the chromium radical after the initial transfer, like the expressions used above (eqs 7 and 8). In this case, a 10% variation in $k_{\text{trH}}/k_{\text{trD}}$ would change S and k_H by 4%. The results are shown in Table 2.

$$S = \frac{{}^{5/6} k_{\text{trD}}[\text{Cr}^\bullet]}{{}^{5/6} k_{\text{trD}}[\text{Cr}^\bullet] + {}^{1/6} k_{\text{trH}}[\text{Cr}^\bullet]} = \frac{5}{5 + k_{\text{trH}}/k_{\text{trD}}} \approx \frac{5}{8} \quad (10)$$

Reaction of (η⁵-C₅H₅)Cr(CO)₃D (1-d₁**) with Methyl Crotonate (**5**), 1-Octene (**6**), (*E*)-2-Methylbut-2-enoic Acid Methyl Ester (**7**), and 2-Methyl-1-heptene (**8**).** The reaction of **1-d₁** (0.03 M) with an excess of **5** (1.0 M) at 323 K in C₆D₆ was extremely slow, with little change in the ¹H NMR spectrum over 10 h. ²H NMR showed little decrease ($\leq 5\%$) in the deuteride resonance of **1-d₁** over 10 h in C₆H₆, and no other deuterium resonance became observable. When, as a control experiment, the stability of **1-d₁** (CpCr(CO)₃D) in C₆H₆ at 323 K was examined, its deuteride resonance showed no decrease over the same period of time. Treating a concentrated solution of **1** (CpCr(CO)₃H, 0.1 M) with 0.5 equiv of **5** (0.05 M) produced a small amount of the hydrogenation product methyl butyrate after 2 days, so the 5% decrease in **1-d₁** in the presence

of excess **5** is probably the result of a small amount of hydrogenation.

In contrast to substrates **2**, **3**, and **4**, which form tertiary radicals (**9-d₁**, **10-d₂**, and **11-d₅** in Schemes 3, 4, and 5) after H•/D• transfer, substrate **5** will give the secondary radical **15-d₁** (Scheme 6). Thus, the initial D• transfer to **5** is less thermodynamically favorable than the transfers above, and therefore slower. However, because **15-d₁** is a relatively uncrowded secondary radical, it accepts a second D• before back transfer can occur. Thus, “hydrogenation” is the exclusive outcome of the reaction of **5** with **1-d₁**. Hydrogenation is also, as some of us have previously reported,⁹ the exclusive outcome of the reaction between CpCr(CO)₃H and styrene, which also generates a secondary radical by the initial H• transfer.

The fast second D• transfer in Scheme 6 contributes a factor of 2 when we write the rate law (eq 11) in terms of the rate constant k_D for the initial D• transfer. The small amount of hydrogenation we have observed gives an upper limit on k_{obs} (eq 12), so k_D at 323 K is $\leq 7.1 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$.

$$-\frac{d[\text{Cr-D}]}{dt} = 2k_D[\mathbf{5}][\text{Cr-D}] = k_{\text{obs}}[\text{Cr-D}] \quad (11)$$

$$0.95 \leq \frac{[\text{Cr-D}]_t}{[\text{Cr-D}]_0} (\text{observed}) = \exp(-k_{\text{obs}}t) \quad (12)$$

Similarly, little reaction occurred when **1-d₁** (0.03 M) was treated with an excess of 1-octene (**6**, 1.0 M) at 323 K in C₆H₆. ²H NMR showed that only about 4% of **1-d₁** had been consumed after 24 h. An analysis like that for **5** implies that k_D for **6** at 323 K is $\leq 2.4 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$.

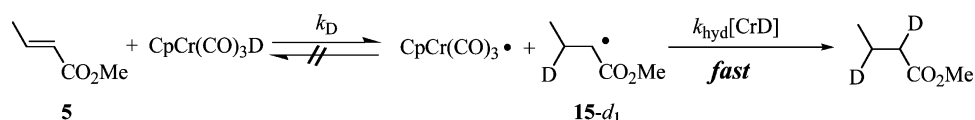
We then examined the reactivities of **7** and **8** (the methyl derivatives of **5** and **6**) so the incipient radicals would be *tertiary* instead of secondary. Treatment of **1-d₁** (0.03 M) with an excess of **7** (the methyl ester of (*E*)-2-methylbut-2-enoic acid, 1.0 M) at 323 K in C₆H₆ gave competing exchange and hydrogenation (Scheme 7). The ²H NMR spectrum showed consumption of 70% of the **1-d₁** in 10 h, with approximately a 50:50 ratio of ²H incorporation into **17/19** (arising from H/D exchange) and **20** (arising from hydrogenation). As shown in Scheme 7, H/D exchange gave only **17** and **19**; no **18** was observed. This result probably reflects the thermodynamic instability of **18** relative to **17**¹⁴ and the reversibility of H•/D• transfer in these reactions.

However, the complexity of the situation makes it impossible to determine an exact value of k_D from the time-dependent NMR data. Neither k_{tr} nor k_{hyd} is known independently. H/D exchange adds to the number of rate expressions that must be considered; e.g., hydrogenation is carried out not only by **1-d₁** but also by **1-d₀** (CpCr(CO)₃H). Six rate constants, related by three kinetic isotope effects (see Scheme S1 in the Supporting Information), would have to be considered in simulating the operation of Scheme 7.

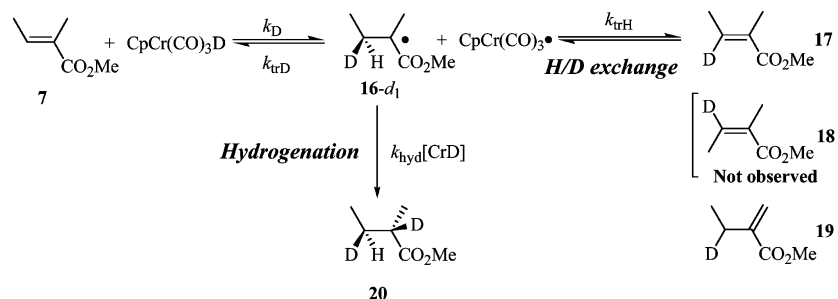
Fortunately, the two limiting expressions, eqs 13–15 for H/D exchange and eq 16 for hydrogenation, produce k_D values that differ only by about a factor of 2. Application of eqs 13–15 to the decline of [**1-d₁**] gives a k_D of $3.6 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, which would be negligibly affected by a 10% variation in $k_{\text{trH}}/k_{\text{trD}}$.

(14) *E*-**7** is 1.38 kcal/mol more stable than *Z*-**7**: J. Franz, Pacific Northwest National Laboratories, personal communication.

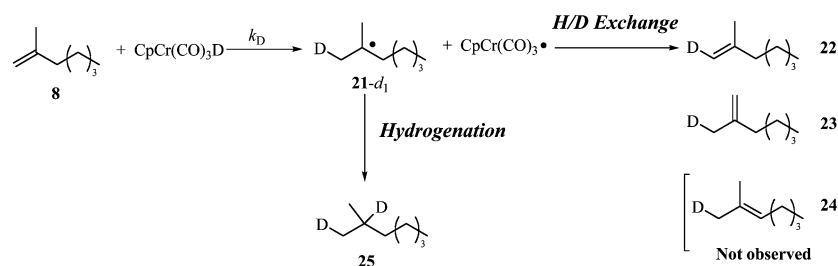
Scheme 6



Scheme 7



Scheme 8



Application of eq 16 to the same data gives a k_D of $1.7 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$.

$$-\frac{d[\text{Cr-D}]}{dt} = k_{\text{obs}}[\text{Cr-D}] \quad (13)$$

$$k_{\text{obs}} = S k_D [7] \quad (14)$$

$$S = \frac{{}^{4/5} k_{\text{trH}}[\text{Cr}^\bullet]}{{}^{1/5} k_{\text{trD}}[\text{Cr}^\bullet] + {}^{4/5} k_{\text{trH}}[\text{Cr}^\bullet]} = \frac{4(k_{\text{trH}}/k_{\text{trD}})}{1 + 4(k_{\text{trH}}/k_{\text{trD}})} \approx \frac{12}{13} \quad (15)$$

$$k_{\text{obs}} = 2k_D [7] \quad (16)$$

When **1-d₁** was treated with an excess of **8** under the same conditions used with **6**, hydrogenation again competed with H/D exchange. The ^2H NMR spectra showed that only 23% of the **1-d₁** had been consumed after 11 h and that the ratio of ^2H incorporation into **22/23** (arising from H/D exchange) and **25** (arising from hydrogenation) was 70:30. The internal double bond isomer **24** was not observed, presumably because the internal hydrogen in the radical **21-d₁** is sterically hindered (see Scheme 8).

Again, the competing reactions make it impossible to determine k_D exactly from the time-dependent NMR data. If we consider the reaction to be an H/D exchange, calculate an observed pseudo-first-order rate constant k_{obs} from the decline in the hydride resonance of **1**, and calculate S from eq 17, we obtain a k_D of approximately $\leq 7.0 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$; the actual

value is presumably lower. A 10% variation in $k_{\text{trH}}/k_{\text{trD}}$ would have a negligible effect on this S and k_D .

$$S = \frac{{}^{5/6} k_{\text{trH}}[\text{Cr}^\bullet]}{{}^{1/6} k_{\text{trD}}[\text{Cr}^\bullet] + {}^{5/6} k_{\text{trH}}[\text{Cr}^\bullet]} = \frac{5(k_{\text{trH}}/k_{\text{trD}})}{1 + 5(k_{\text{trH}}/k_{\text{trD}})} \approx \frac{15}{16} \quad (17)$$

Discussion

Comparison of H $^\bullet$ Transfer Rate Constants: Influence of Olefin Structure. In order to compare the H $^\bullet$ -accepting ability of the various olefins, we need to be able to estimate k_{H} (from $\text{CpCr}(\text{CO})_3\text{H}$) when we have measured k_D (from $\text{CpCr}(\text{CO})_3\text{D}$). Inverse isotope effects are generally observed for the transfer of H $^\bullet$ from M–H to a carbon–carbon double bond.^{8,15} The only isotope effect reported for $\text{CpCr}(\text{CO})_3\text{H}$, by Bullock et al.,⁷ is $k_{\text{HCr}}/k_{\text{DCr}} = 0.45 \pm 0.10$ for its reaction with 2-cyclopropylpropene at 341 K. It seems appropriate to take 0.45 as a conversion factor, despite the small difference in temperature,¹⁶ and we have done so in Table 3.










$$k_{\text{H}} = k_D \frac{k_{\text{HCr}}}{k_{\text{DCr}}} \quad (18)$$

There have been numerous kinetic studies of free radical additions to multiple bonds.^{17,18} However, there is comparatively little information on the relative rates at which various olefins

(15) It has been suggested⁸ that such inverse isotope effects are the consequence of a two-step mechanism for H $^\bullet$ transfer, with a fast H $^\bullet$ transfer equilibrium inside a solvent cage followed by slow diffusion out of the cage.

(16) The effect of the temperature difference is insignificant compared to the uncertainty in our rate constants.

Table 3. Rate Constants k_H for H• Transfer from (η^5 -C₅H₅)Cr(CO)₃H to Various Substituted Olefins at 323 K

		k_H ($\times 10^{-3}$ M ⁻¹ s ⁻¹)	relative rate
2 ^b		0.59 (2)	1
3		460 (60)	780
4		79 (3)	134
5 ^b		$\leq 3.2 \times 10^{-4}$	$\leq 5 \times 10^{-4}$
6 ^b		$\leq 1.1 \times 10^{-4}$	$\leq 2 \times 10^{-4}$
7 ^b		$(0.8-1.6) \times 10^{-2}$	~ 0.02
8 ^b		$\leq 3.2 \times 10^{-3}$	≤ 0.005
styrene		15.8 (6) ^a	27
MMA		14 (3) ^a	24

^a From our previous work.⁹ ^b Obtained from measured k_D by eq 18.

accept H• from a hydride complex. Roth and co-workers have reported rate constants for the stoichiometric hydrogenation of several styrenes by HCo(CO)₄.^{4d} Masuyama and co-workers have recently used competition experiments to compare the reactivity of alkenes in a reaction that probably involves H• transfer from Co, the Co(II)-catalyzed formation of trimethylsilyl peroxides from O₂ and Et₃SiH.¹⁹ However, there has been no previous *direct* measurement of rate constants for H• transfer to olefins with a variety of substituents.

The reactivity of an olefin toward a free radical is largely determined by three factors: (a) the ΔH of the reaction, (b) the extent of steric congestion on the radical and the olefin, and (c) polar effects. We would expect similar factors to determine the rate at which an olefin can accept H• transfer from a transition-metal hydride. Comparison of **4**, **8**, and MMA in Table 3 shows that additional substituents on propylene affect its reactivity in the order Ph (**4**) > CO₂Me > alkyl (**8**), with the reactivity ratio being about 24,000:4000:1. The sluggishness of **8** can be attributed to the high energy of the radicals that would be generated by H• transfer. A tertiary radical with only alkyl substituents forms a C–H bond with a strength of 96.7 kcal/mol; the introduction of a carbomethoxy substituent, for example in (MeO₂C)(CH₃)₂C–H, weakens the bond to 85 kcal/mol,^{20,21} while the introduction of a phenyl substituent, for example in Ph(CH₃)₂C–H, weakens it to 84.4 kcal/mol.^{20,22}

As the data in Table 3 show, the methyl substituent in **4** increases its reactivity over that of styrene by a factor of 5; the methyl substituent in **7** increases its reactivity over that of **5** by a factor of about 40; the methyl substituent in **8** increases its

reactivity over that of **6** by a factor of about 30. In general, a methyl substituent on the incipient radical site increases the H• transfer rate 5–50 times.

The additional phenyl substituent in **3** increases its reactivity over that of styrene by a factor of about 30—a bigger increase than that produced by the additional methyl substituent in α -methylstyrene (**4**), which is only 5 times more reactive than styrene. These results reflect the ability of phenyl substituents to stabilize radicals: the replacement of the italicized hydrogen in Ph(CH₃)(H)C–H by phenyl weakens the C–H bond by 4.4 kcal/mol, whereas the replacement of the same hydrogen by methyl weakens the C–H bond by only 3.4 kcal/mol.^{20,22} Thus, *the stability of the incipient radical plays an important role in determining the rate of such H• transfer reactions.*

The data in Table 3 also show that a methyl substituent on the carbon that receives the H• slows down the rate of H• transfer significantly: **2** is about 800 times less reactive than **3**, and **7** is about 1200 times less reactive than MMA. The effect is obviously steric and not unexpected from the literature. In their investigation of the hydrogenation of styrenes by HCo(CO)₄, which occurs by an H• transfer mechanism, Roth and co-workers^{4d} found little reaction when there were β -methyl substituents. Similarly Connolly,^{4e} when studying the transfer of H• from HFe(CO)₄SiCl₃ to dienes, found no observable reaction when both ends of the diene were substituted.

Experimental Section

General. All air-sensitive materials were prepared and handled under an argon or nitrogen atmosphere using standard Schlenk techniques or an inert atmosphere box. THF, benzene, C₆D₆, and toluene-*d*₈ were distilled under N₂ from Na/benzophenone. Et₂O and hexane were deoxygenated and dried with two successive activated alumina columns under Ar.²³ Other chemicals were deoxygenated by purging with N₂ or degassed by freeze–pump–thaw procedures. Commercial methyl crotonate (**5**) was dried by CaH₂; 1-octene (**6**) and 2-methyl-1-heptene (**8**) were dried by sodium. Hexamethylcyclotrisiloxane was purified by vacuum transfer and used as an internal standard in NMR kinetics experiments.

Materials. 1,1-Diphenylpropene (**2**),²⁴ 1,1-diphenylethylene-2,2-*d*₂ (**3-*d*₂**),²⁵ (*E*)-2-methylbut-2-enoic acid methyl ester (methyl tiglate, **7**),²⁶ and CpCr(CO)₃H (**1**)²⁷ were prepared as described in the literature.

CpCr(CO)₃D. A slight modification of the literature procedure²⁸ was employed. D₃PO₄ (0.15 mL, 85% in D₂O, 99% *d*) was added to a solution of 0.22 g of Na[CpCr(CO)₃]²⁹ (1 mmol) in 10 mL of THF. After 45 min of stirring, THF was removed in vacuo, and the remaining green powder was sublimed onto a dry ice/acetone-cooled sublimation probe. A 54% yield of CpCr(CO)₃D (0.11 g) was obtained. The isotopic purity was >90%.

α -Methylstyrene-*d*₅ (4-*d*₅**)** was prepared by a slight modification of the literature procedure.³⁰ Acetone-*d*₆ was treated with phenylmagnesium bromide, and the product was dehydrated with *p*-toluenesulfonic acid in warm benzene to afford **4-*d*₅** (>99% D).³¹

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 (31) Decrease of deuterium content in **4-*d*₅** was observed under prolonged reaction times or at high temperatures.

Reaction of $\text{CpCr}(\text{CO})_3\text{H}$ (or **D) with Olefins.** In preliminary experiments, the concentrations of the olefins and **1** (or **1- d_1**) were varied to determine the reaction time and temperature suited for measuring k_{H} (or k_{D}) accurately. An excess of olefin (>10 -fold over **1** or **1- d_1**) was always employed. In most kinetic experiments, C_6D_6 or C_6H_6 (for ^2H NMR) was used as a solvent. For the reaction of $\text{CpCr}(\text{CO})_3\text{H}$ with 1,1-diphenylethylene-2,2- d_2 , toluene- d_8 was used because of the low temperatures required.

NMR Kinetic Measurements. All such experiments were performed at 300 MHz. A stock solution of **1** or **1- d_1** was prepared with the internal standard (hexamethylcyclotrisiloxane), placed in a J-Young tube, and frozen under an atmosphere of N_2 . A solution of the olefin was then added to the same tube and also frozen under N_2 . The tube was allowed to thaw, and its contents were mixed before it was placed in the probe of the NMR (whose temperature controller was already set to the desired temperature). Ethylene glycol (for $T > 300$ K) and methanol (for $T < 300$ K) standards were used to calibrate the controller.

The height of the hydride or deuteride peak (relative to the internal standard) was recorded as a function of time. When the reaction was monitored by ^1H NMR, two pulses were generally used for each kinetic point, with 10 s between the two pulses; however, for the reaction of 1,1-diphenylethylene-2,2- d_2 with **1**, only a single pulse was used (due to the speed of the reaction). The kinetic data were fit to an exponential, and the rate constant and the infinity point were adjusted for the best

fit. The activation parameters were obtained from a linear fit to the Eyring equation, and the values of k_{H} at 323 K were extrapolated from that equation; the uncertainties given for the extrapolated k_{H} values take into account covariance between ΔH^\ddagger and ΔS^\ddagger .

For ^2H NMR kinetics in C_6H_6 , the $\text{C}_6\text{H}_5\text{D}$ resonance was used as an internal standard,³² with 400 pulses (separated by a delay of 100 ms) used to obtain each kinetic point.

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Supporting Information Available: Details of $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{D}/1,1$ -diphenylpropene isotope exchange, details of isotope exchange between $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})_3\text{H}$ and 1,1-diphenylethylene-2,2- d_2 or α -methylstyrene- d_5 , and a complete list of the reactions required for the simulation of Scheme 7. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(32) The concentration of deuterium in C_6H_6 from the natural abundance of ^2H is approximately 0.01 M.