Kinetics and Mechanism of the Formation of Organochromium(III) Complexes in the Reactions of Organic Peroxides with Chromium(II)[1]

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Abstract: Bimolecular rate constants for reduction of a series of 17 organic peroxides, hydroperoxides, peresters, and peroxyacids by Cr^{2+} vary within the range 7.7×10^{-6} to 3×10^6 M^{-1} s^{-1} (25° in 1:1 v/v CH_3OH/H_2O). Steric factors provide the dominant influence upon reactivity, whereas electronic effects are relatively unimportant. Reaction products in both CH_3OH/H_2O and in aqueous solution are consistent with the formation of alkoxy-radical intermediates. Organochromium(III) species, $(H_2O)_5CrR^{2+}$, are detected in all but the slowest reactions. The observation of a transient intermediate in reaction of perbenzoic acid with Cr(II) is attributed to formation and decomposition of phenylchromium(III) ion.

Reduction of hydrogen peroxide by a variety of metal ions including Fe^{2+},[2] Ti^{III},[3] Cr^{2+},[3] and VO^{2+} [3] indicates that reaction occurs at least in part by a successive one-electron-transfer mechanism.

$$M^{n+} + HOOH \xrightarrow{H^+} M^{(n+1)+} + \cdot OH \qquad (1)$$

$$M^{n+} + \cdot OH \xrightarrow{H^+} M^{(n+1)+} + H_2O \qquad (2)$$

Addition of organic substrates RH to these "Fenton-like" reagents[4] diverts hydroxyl radical in reaction 2 to produce organic radicals via reaction 3,

$$RH + \cdot OH \rightarrow R\cdot + H_2O \qquad (3)$$

providing an excellent route into the study of these latter species.[5]

More recently, chemical and radiolytic generation of carbon-centered radicals have been adapted to prepare organochromium(III) species, via radical capture by Cr^{2+}.[6,7] Similar complexes of the formula $(H_2O)_5CrR^{2+}$ have been proposed[8] and sometimes detected[9] in the reactions of Cr^{2+} with a number of organic peroxides. There is presently available a good deal of information concerning reaction products in these systems.[10] However, with few exceptions[10] kinetic data have not been reported concerning the rates and mechanism of interaction between Cr^{2+} and organic peroxides. Our own interest in the preparation and chemistry of organochromium(III) complexes[11] prompted an investigation into the factors affecting the reactions between various organic peroxides (a term we use to include peroxides, hydroperoxides, peroxyacids, and peresters), particularly the generation of CrR^{2+} complexes thereby. Details are reported herein.

Formation of the strongly absorbing organochromium(III) species has proven to be an extremely useful kinetic probe, facilitating study of peroxide reactions with chromium(II) where previously the necessarily poorer quality of data has been shown to be restrictive.[3]

Experimental Section

Preparation of Organic Peroxides and Other Reagents. A number of the peroxides used in this study were commercially available: *tert*-butyl hydroperoxide, di-*tert*-butyl peroxide, and *tert*-butyl perbenzoate (Matheson, Coleman and Bell) and benzoyl peroxide (Aldrich Chemical Co.). Other samples including some of the above, were prepared by methods available in the literature: ethyl *tert*-butyl peroxide and isopropyl *tert*-butyl peroxide,[12] cumene hydroperoxide,[13] α,α-dimethyl β-phenethyl hydroperoxide,[9] *n*-butyl hydroperoxide,[14] *sec*-butyl hydroperoxide,[15] *tert*-amyl hydroperoxide,[16] substituted *tert*-butyl perbenzoates,[17] and perbenzoic acid.[18] The characterization and purity of samples were checked by NMR spectroscopy, boiling points of samples (as cited in the literature), elemental analysis where possible, and always by peroxide assay, using iodometric titration.[19] In all cases the compounds used satisfied the known data, and were sufficiently pure, after vacuum distillation, for kinetic runs. Samples of the neat compounds were stored at −10° when not in use, and solutions were always freshly made prior to reaction.

Solutions of $Cr(ClO_4)_2$ were prepared by reduction of chromium(III) perchlorate with amalgamated zinc under a nitrogen atmosphere in dilute aqueous perchloric acid.

Kinetic Experiments. Preliminary runs in a variety of mixed solvents, for example, THF/H_2O, C_2H_5OH/H_2O, and CH_3OH/H_2O, provided evidence for hydrogen atom abstraction from the solvent by radicals produced during the course of reaction. A strictly aqueous solution would eliminate this problem, but this was unfortunately not feasible owing to the very limited solubility of many of these peroxides. Hence it was necessary to employ a mixed-solvent system, although as reported herein, some important product distribution data were obtained in a strictly aqueous medium.

A 1:1 v/v CH_3OH/H_2O solvent was chosen as the standard kinetic solvent, with runs being conducted under an atmosphere of Cr^{2+}-scrubbed nitrogen with ionic strength maintained at 1.0 M with $LiClO_4$ and $HClO_4$. Runs were carried out at 25° unless stated otherwise. A Durrum stopped-flow spectrophotometer was employed for many kinetic runs, and in the case of the slower reactions a Cary 14 spectrophotometer was used. For the slower reactions, particularly those of ethyl *tert*-butyl peroxide and isopropyl *tert*-butyl peroxide, conditions had to be carefully chosen to avoid interference from the slow acidolysis of the organochromium products. In such cases the growth of Cr^{3+} was monitored through the small absorbance increases at λ 400–410 nm, although in most instances the reaction was followed by monitoring large absorbance increases at appropriate wavelengths corresponding to absorption maxima for the organochromium(III) species, generally between 260 and 390 nm.

With the exception of the reaction of Cr^{2+} with perbenzoic acid, whose rate was so high that second-order conditions were required, the reactant concentrations were selected with a 10- to 50-fold excess of Cr^{2+} over peroxide. The concentration of Cr^{2+} in run solutions was determined by reaction with $Co(NH_3)_5Cl^{2+}$, determining Co^{2+} as the thiocyanate complex in 50% acetone–water at λ 623 nm (ϵ 1.84×10^3 M^{-1} cm^{-1}).

Kinetic Data. Conventional pseudo-first-order rate plots were constructed to permit computation of a rate constant designated k_{obsd}. An exception to this was made in a few cases where the product decomposition rate was not negligibly slow compared to its formation, in which instance a consecutive reaction scheme or Swinbourne's method[20] was used to obtain a self-consistent set of kinetic data.

We here assume, and will later verify, that in every instance the rate-limiting step is the simple bimolecular process of eq 4, followed by numerous and varied rapid reactions of the radical so generated.

$$Cr^{2+} + ROOR' \xrightarrow{k_1} [CrOR']^{2+} + RO\cdot \qquad (4)$$

Table I. Kinetic Data for the Reduction of Organic Peroxides ROOR′ by Chromium(II), 25.0°, μ = 1.00 M ($LiClO_4$) in 1:1 v/v CH_3OH/H_2O

	Range of initial concentration			
ROOR	[ROOR′]/M	$[Cr^{2+}]$/M	λ/nm	$k_1/M^{-1}\ s^{-1}$ (no.)[a]
t-BuOO-t-Bu	1.7×10^{-2}	3.3×10^{-1}	408	$\leq 7.7 \times 10^{-6}$ (1)[b,c]
t-BuOOCH$(CH_3)_2$	$(1.2–6.0) \times 10^{-3}$	$(2.20–10.0) \times 10^{-2}$	408	$(4.19 \pm 0.40) \times 10^{-2}$ (7)
t-BuOOC_2H_5	$(0.50–1.00) \times 10^{-3}$	$(0.71–4.50) \times 10^{-2}$	258, 390	2.35 ± 0.25 (16)
t-BuOOH	$(1.50–3.00) \times 10^{-4}$	$(0.61–7.51) \times 10^{-3}$	258, 392	$(1.65 \pm 0.11) \times 10^{4}$ (20)
$C_2H_5C(CH_3)_2OOH$	$(1.0–2.0) \times 10^{-4}$	$(0.81–7.30) \times 10^{-3}$	275, 394	$(1.60 \pm 0.11) \times 10^{4}$ (14)
$PhC(CH_3)_2OOH$	$(0.50–3.00) \times 10^{-4}$	$(0.55–6.13) \times 10^{-3}$	258	$(0.99 \pm 0.06) \times 10^{4}$ (19)
$PhCH_2C(CH_3)_2OOH$	$(1.4–2.8) \times 10^{-4}$	$(0.48–7.53) \times 10^{-3}$	297, 358	$(2.13 \pm 0.18) \times 10^{4}$ (22)
n-BuOOH	$(0.50–1.00) \times 10^{-4}$	$(0.40–5.05) \times 10^{-3}$	260, 280	$(5.77 \pm 0.43) \times 10^{4}$ (16)
sec-BuOOH	$(0.50–1.00) \times 10^{-4}$	$(0.59–5.03) \times 10^{-3}$	275, 330	$(3.63 \pm 0.61) \times 10^{4}$ (16)
PhC(O)OOH	$(2–4) \times 10^{-5}$	$(0.89–1.90) \times 10^{-4}$	260, 280	$(3.3 \pm 0.5) \times 10^{6}$ (8)
PhC(O)OOC(O)Ph	$(1.0–3.0) \times 10^{-4}$	$(0.53–6.03) \times 10^{-2}$	392, 580	$(5.2 \pm 0.2) \times 10^{1}$ (16)[c]
t-Bu-OOC(O)Ph	$(0.50–1.50) \times 10^{-4}$	$(0.73–7.58) \times 10^{-3}$	288, 392	$(1.18 \pm 0.09) \times 10^{4}$ (14)
t-Bu-OOC(O)-p-ClC_6H_4	$(2.98–5.58) \times 10^{-3}$	$(3.6–7.0) \times 10^{-4}$	300	$(8.9 \pm 1.1) \times 10^{3}$ (4)[d]
t-Bu-OOC(O)-m-ClC_6H_4	$(1.01–7.9) \times 10^{-3}$	$(3.4–10.1) \times 10^{-4}$	300	$(1.02 \pm 0.13) \times 10^{4}$ (4)[d]
t-Bu-OOC(O)-p-$CH_3OC_6H_4$	$(1.02–10.2) \times 10^{-3}$	$(3.6–10.1) \times 10^{-4}$	300	$(1.50 \pm 0.12) \times 10^{4}$ (4)[d]
t-Bu-OOC(O)-m-$CH_3C_6H_4$	$(1.0–8.7) \times 10^{-3}$	$(3.5–10.0) \times 10^{-4}$	300	$(1.23 \pm 0.04) \times 10^{4}$ (4)[d]
t-Bu-OOC(O)-p-NCC_6H_4	$(1.02–8.55) \times 10^{-3}$	$(3.4–10.1) \times 10^{-4}$	300	$(8.2 \pm 0.1) \times 10^{3}$ (4)[d]

[a] The mean value of k_1, the standard deviation, and the number of determinations in parentheses. [b] One run at 23°, assuming a first-order dependence upon $[Cr^{2+}]$. [c] Experimental k_1 divided by a statistical factor of 2 for this symmetrical compound. [d] Reference 45.

Some but by no means all of the subsequent reactions produce an organochromium(III) species. Provided the overall stoichiometry 1 peroxide:2 Cr^{2+} is maintained, *the yield of organochromium complex does not affect the determination of* k_1, *which is given by* $k_{obsd}/[Cr^{2+}]$ *regardless of the fraction of the intermediate one of whose rapid reactions yields that particular product whose absorbance is being used to monitor the reaction rate.* That is to say, the concentration of a particular organochromium product $[P_i]$ is given by the relation

$$[P_i]/[\text{peroxide}]_0 = f_i[1 - \exp(-k_1[Cr^{2+}]t] \qquad (5)$$

where f_i represents the fraction of the radical intermediate yielding the product P_i; clearly, only the yield of P_i, and not the specific reaction rate, depends upon f_i.

Product Identification. Three different approaches were adopted, depending on the information required: (1) Ion exchange separation was used in a few reactions to identify the Cr(III) complexes, and proved particularly useful for the products CrO_2CPh^{2+}, $Cr(C_2H_5OH)^{3+}$, and $Cr(t\text{-}BuOH)^{3+}$ as well as some organometallic products. The separations were effected by transferring reacted solutions onto a column of Dowex 50W-X8 cation exchange resin in the Li^+ form, followed by elution with appropriate combinations of $LiClO_4$ and $HClO_4$, up to 4 M $HClO_4$, and ultimately using 3 M H_2SO_4 to remove the tightly bound tripositive Cr(III) complexes with coordinated alcohols. (2) Measurement of the acidolysis rate of the organochromium product produced from reactions in 50% CH_3OH/H_2O provides in most cases an unambiguous identification, largely because the products of all 17 reactions produced one of five possible alkyl derivatives, each of which is known from independent unambiguous reactions.[7,9,11a,c] Comparison of the products formed in strictly aqueous solvent, whenever solubility considerations permitted, afforded additional information on the reactions of radical intermediates. (3) Mass spectrometric investigations of volatile products of reaction of perbenzoic acid were also carried out.

Results

Kinetics of Cr^{2+} Reductions. Reduction of each of the organic peroxides by Cr^{2+} conforms strictly to a second-order rate expression, given by eq 6:[21]

$$-d[ROOR']/dt = k_1[ROOR'][Cr^{2+}] \qquad (6)$$

Plots of ln $(D_\infty - D_t)$ vs. time were linear for at least three half-lives throughout, and k_1 proved independent of $[H^+]$ in the range 0.05 M $\leq [H^+] \leq$ 1.0 M. Typical data for the Cr^{2+} reduction of *tert*-butyl hydroperoxide, *sec*-butyl hydroperoxide, and *n*-butyl hydroperoxide are shown in Figure 1 plotted as k_{obsd} vs. $[Cr^{2+}]$. These plots are linear within experimental error and pass through the origin, in conformity with eq 6. The slopes of these lines afford the values k_1, which are summarized along with the experimental conditions in Table I for all 17 peroxides studied.

On the basis of the absorbance changes measured in the kinetic runs,[22] the yields of the $(H_2O)_5CrR^{2+}$ products based on the limiting initial quantity of peroxide were typically 10–20% of theoretical for the situation in which 100% of the alkoxy radical RO· led to the formation of an organometallic product.

Kinetics of Organochromium(III) Decomposition. Each of the organochromium(III) products undergoes slow decomposition corresponding to an acidolysis process resulting in Cr–C bond cleavage as shown in eq 7.

$$CrR^{2+} + H_3O^+ = Cr^{3+}_{aq} + RH \qquad (7)$$

Preliminary experiments showed that the rate constant for a given decomposition reaction was the same whether or not the complex was first isolated from the reaction solution by ion-exchange chromatography. These determinations were made using the CrR^{2+} complexes derived from the reaction of *tert*-butyl hydroperoxide in each of two solvents, H_2O (producing $CrCH_3^{2+}$) and CH_3OH/H_2O (producing $CrCH_2OH^{2+}$).[23] Consequently in subsequent reactions the rate of decomposition of the CrR^{2+} product was determined directly in the solution immediately after completion of the peroxide reaction, by simply air-oxidizing the residual Cr^{2+}.

Conditions for these experiments were chosen such that substantial absorbance changes could be monitored, principally around λ_{max} 380–390 nm,[24] with $[ROOR'] \cong 2\text{–}5 \times 10^{-3}$ M, $[Cr^{2+}]_0 \cong 1\text{–}3 \times 10^{-2}$ M, at μ = 1.00 M ($LiClO_4$) and 25.0°. Pseudo-first-order plots of ln $(D_t - D_\infty)$ vs. time were linear to at least 80% completion. A general expression for the rate of reaction 7 is

$$-d[CrR^{2+}]/dt = (k_2 + k_3[H^+])[CrR^{2+}] \qquad (8)$$

although for R = CH_3 no k_2 term was observed. Plots of k_{obsd} vs. $[H^+]$ are shown in Figure 2 for the three major organochromium products, R = CH_3, CH_2OH, and C_2H_5. Each point in the figure is keyed to the organochromium(III) cations listed in Table II, the major *identification* of the CrR^{2+} product

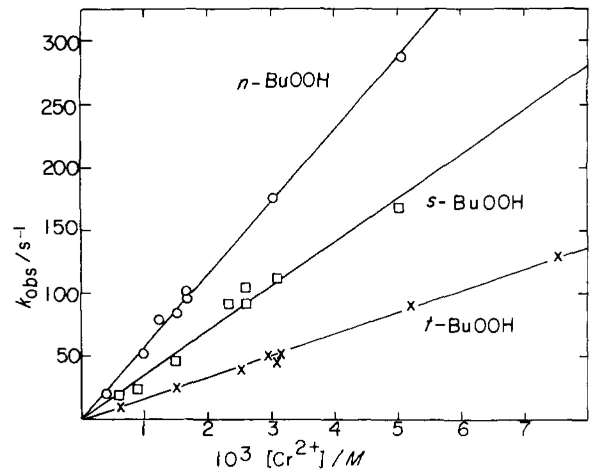


Figure 1. Plots of pseudo-first-order rate constant vs. $[Cr^{2+}]$ for reduction of three typical hydroperoxides.

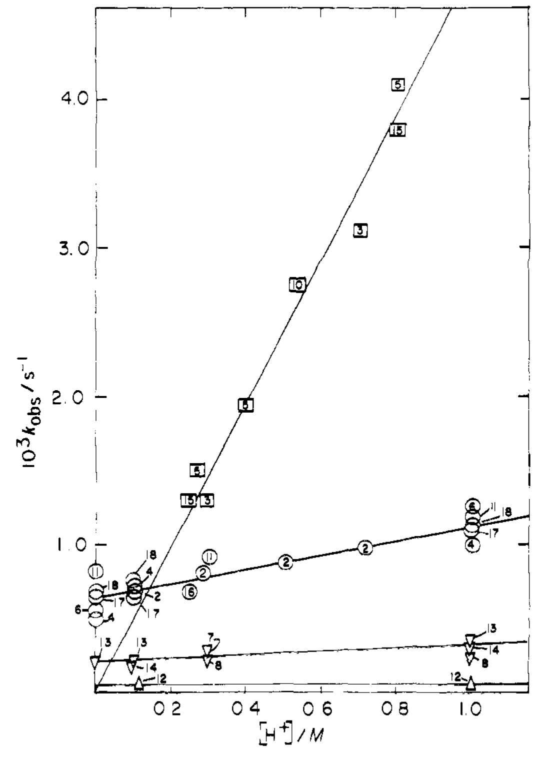


Figure 2. Plots of rate constants for acidolysis of the four organochromium(III) reaction products against $[H^+]$. The number designations refer to the reactions as given in Table III.

Table II. Identity[a] of Organochromium(III) Products

Oxidant source ROOR′	Product[b]	
	In aq H_3O^+	In 1:1 CH_3OH/H_2O
H_2O_2	Cr^{3+}_{aq} (1)	$CrCH_2OH^{2+}$ (2)
t-BuOOH	$CrCH_3^{2+}$ (3)	$CrCH_2OH^{2+}$ (4)
$PhC(CH_3)_2OOH$	$CrCH_3^{2+}$ (5)	$CrCH_2OH^{2+}$ (6)
$C_2H_5C(CH_3)_2OOH$	$CrC_2H_5^{2+}$ (7)	$CrC_2H_5^{2+}$ (8)
$PhCH_2(CH_3)_2OOH$	$CrCH_2Ph^{2+}$ [c]	$CrCH_2Ph^{2+}$ [d]
t-$BuOOC_2H_5$	$CrCH_3^{2+}$ (10)	$CrCH_2OH^{2+}$ (11)
n-BuOOH	$Cr(CH_2)_4OH^{2+}$ (12)	---
sec-BuOOH	$CrC_2H_5^{2+}$ (13)	$CrC_2H_5^{2+}$ (14)
t-BuOOC(O)Ph	$CrCH_3^{2+}$ (15)	$CrCH_2OH^{2+}$ (16)
PhC(O)OOC(O)Ph	---	$CrCH_2OH^{2+}$ (17)
PhC(O)OOH	$CrC_6H_5^{2+}$ [e]	$CrCH_2OH^{2+}$ (18)

[a] The organochromium product from the particular ROOR′ + Cr^{2+} reaction in the respective solvent. [b] Each product is keyed by the parenthetical number to the experiment(s) on acidolysis illustrated in Figure 2. [c] From its uv-visible spectrum with λ_{max} 355 nm. [d] The product in CH_3OH/H_2O was not determined but earlier work[9] identified this product in C_2H_5OH/H_2O solutions. [e] The presumed product from perbenzoic acid + Cr^{2+} in 100% aqueous solution (see text).

Table III. Values of Rate Constants k_2 and k_3 for Acidolysis of Organochromium(III) Cations, eq 7 and 8[a]

CrR^{2+}	k_2/s^{-1}	$k_3/M^{-1}\,s^{-1}$	No.[b]
$CrCH_3^{2+}$	---	4.94×10^{-3} [c]	4
$CrC_2H_5^{2+}$ [d]	2.2×10^{-4}	1.15×10^{-4}	4
Cr-n-$C_3H_7^{2+}$ [e]	3.0×10^{-4}	6.5×10^{-5}	0
$CrCH_2OH^{2+}$	6.6×10^{-4} [f]	4.65×10^{-4} [f]	6
$Cr(CH_2)_4OH^{2+}$	6.12×10^{-5}	---	1
$CrC_6H_5^{2+}$ [g]	1.3	1.64×10^3	1

[a] At μ = 1.0 M ($LiClO_4$, $HClO_4$) in mixed aqueous methanol containing from 0 to 50 vol % CH_3OH. [b] The number of different peroxide systems which produce the particular CrR^{2+} product. [c] Reference 6 gives $k_3 = 5.0 \times 10^{-3}$ $M^{-1}\,s^{-1}$. [d] Determined on authentic and purified $CrC_2H_5^{2+}$ by Mr. T. J. McNeese. [e] Determined on authentic Cr-n-$C_3H_7^{2+}$ by Mr. M. J. Haasl. [f] Reference 7b gives $k_2 = 7 \times 10^{-4}\,s^{-1}$ and $k_3 = 3.2 \times 10^{-4}$ $M^{-1}\,s^{-1}$. [g] The presumed product from benzoic acid + Cr^{2+} in 100% aqueous solution (see text).

formed in each instance being just this agreement between the rate constant at a particular $[H^+]$ compared to that for the authentic compound. The products so identified are given in Table II, and in Table III are listed values of k_2 and k_3 for these and related complexes.

Ion-Exchange Separations. Further separations and product identifications were carried out in three systems, t-BuOOH, t-$BuOOC_2H_5$, and t-BuOOC(O)Ph.

For the first of these, reaction with Cr^{2+} was carried out in both 1:1 CH_3OH/H_2O and in aqueous solution. The former, after ion-exchange separation, yielded a dipositive organochromium(III) cation with λ_{max} 390 nm; the complex underwent acidolysis at the same rate as authentic $CrCH_2OH^{2+}$. No $CrCH_3^{2+}$ was detected in this experiment, and its concentration can conservatively be estimated as <5% of that of $CrCH_2OH^{2+}$. A 15% absolute yield of $CrCH_2OH^{2+}$ was determined from the absorption spectrum[25] prior to separation.

The reaction in aqueous perchloric acid produced $CrCH_3^{2+}$, which could be eluted from the resin column by 1 M $LiClO_4$ at 0°. The complex, produced in 10–15% yield, was characterized by its decomposition rate and by its spectrum.[26]

The assumed rate-limiting step, generalized in eq 4, implies that reaction of t-$BuOOC_2H_5$ with Cr^{2+} should produce, in the first step, a Cr(III) product containing a single molecule of coordinated ethanol along with the *tert*-butoxy radical (the latter leading eventually to the organochromium product).[27] The O-coordinated monoethanol complex $(H_2O)_5CrO(H)C_2H_5^{3+}$ has been characterized by Kemp and King,[28] the ethanol content being determined through Cr(VI) oxidation to acetic acid.

The elution pattern of the products of the reaction carried out in strictly aqueous perchloric acid[29] showed no $Cr(H_2O)_6^{3+}$ (as expected), but resulted in a more tightly held 3+ ion, which was analyzed to contain 0.7 ± 0.1 coordinated ethanol per chromium(III). The low result we presume is due to simultaneous elution of some of the t-BuOH complex.

The reaction of *tert*-butyl perbenzoate (10^{-2} M) with Cr^{2+} (0.04 M) in aqueous perchloric acid (0.05 M) was allowed to proceed for sufficient time to complete the acidolysis of

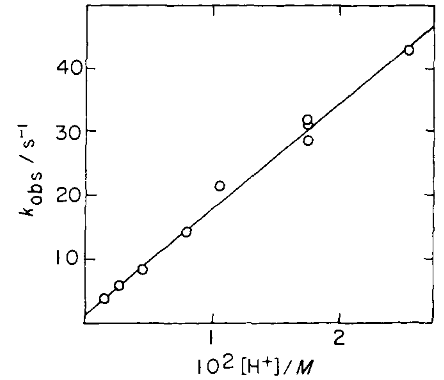


Figure 3. Kinetic data for the second stage of reaction of perbenzoic acid with Cr^{2+}, which is attributed to the acidolysis of $CrC_6H_5^{2+}$

$CrCH_3^{2+}$, following which excess Cr^{2+} was air oxidized and the solution transferred to the ion-exchange column. Elution with 0.5 M $HClO_4$ produced a dipositive, green Cr(III) complex with absorption maxima at 412 and 585 nm. The peak positions and relative intensities of this spectrum compare closely to an authentic sample of the complex $(H_2O)_5CrO_2CC_6H_5^{2+}$.[30] The yield was not reliably determined, however, in that the green complex decomposes[31] over a period of time forming products identified as $Cr(H_2O)_6^{3+}$ and free benzoic acid.

Reaction of Perbenzoic Acid with Cr^{2+} and Detection of Phenylchromium Ion. When reaction is carried out in CH_3OH/H_2O solvent, there is formed a moderately stable organochromium(III) product identified as $CrCH_2OH^{2+}$ by its rate of acidolysis (Table II and Figure 2). In the strictly aqueous solution, however, a transient intermediate ($CrC_6H_5^{2+}$?) is detected spectrally. The rate of its decomposition varies linearly with [H^+], as shown in Figure 3. This rate law is in accord with that for the acidolysis of the other CrR^{2+} complexes, but the values of k_2 and k_3 are much higher here than for the alkyl derivatives. The decomposition rate is independent of Cr^{2+} (0.007-0.021 M), consistent with its formulation as $CrC_6H_5^{2+}$. The approximate absorption spectrum[32] (shown in Figure 4), exhibits a shoulder at 310 nm.

Further experiments were conducted to determine the volatile products using mass spectrometry.[33] Immediately upon mixing (perbenzoic acid added to Cr^{2+}, the latter in twofold stoichiometric excess) strong signals from the products CO_2 and C_6H_6 were noted. The mass spectrum was consistent with just these two volatile components. No evidence for benzoic acid or biphenyl could be seen. Addition of a known amount of benzene-d_6 to the perbenzoic solution prior to reaction enabled an estimate for benzene yield at 1.8 ± 0.3% based on initial $C_6H_5CO_3H$.

Attempts to further confirm the identity of $CrC_6H_5^{2+}$ by its reaction with Hg^{2+} were thwarted by an interaction between the latter and perbenzoic acid which occurs during the time necessary to prepare the solutions and fill the stopped-flow apparatus.

Interpretation and Discussion

Reaction Mechanism. Hydrogen peroxide is reduced rapidly by Cr^{2+} in aqueous acidic solution ($k_{H_2O_2} = (2.8 \pm 0.7) \times 10^4$ M^{-1} s^{-1} at 25° [3,34]). Available evidence supports a mechanism involving successive one-electron transfer steps.[3,35,36] The initial reaction step in this case is considered to be radical abstraction,[3] producing the hydroxyl radical (eq 9), and the corresponding reactions of organic peroxides occur analogously as shown in eq 10.

$$H_2O_2 + Cr^{2+} \rightarrow CrOH^{2+} + OH\cdot \qquad (9)$$

$$ROOH + Cr^{2+} \xrightarrow{k_1} CrOH^{2+} + RO\cdot \qquad (10)$$

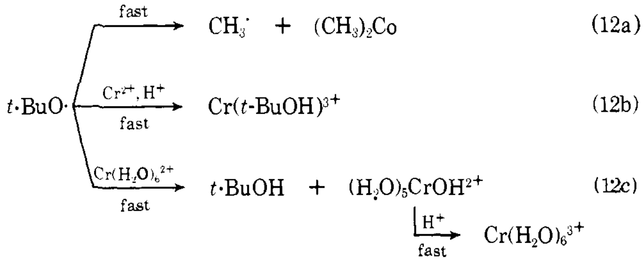
The bimolecular rate constants k_1 for the Cr^{2+} reduction of the series of organic peroxides described herein lie both above and below that for hydrogen peroxide, and span some 11 orders of magnitude (Table I).

The mechanism of reaction is believed to be essentially the same throughout the series, although the site of Cr^{2+} attack depends upon the reactant structure. It is perhaps instructive to consider at this point one representative member of the series. For this reason we have chosen to discuss the reaction of Cr^{2+} with ethyl *tert*-butyl peroxide (C_2H_5OO-*t*-C_4H_9) in detail. This particular peroxide, being unsymmetrical, affords products which provide a good indication of the site of initial attack. In dilute perchloric acid, in strictly aqueous solvent, the primary reaction products have been identified as $CrCH_3^{2+}$ and the monoethanol complex $(H_2O)_5CrO(H)C_2H_5^{3+}$. These products rather clearly indicate that initial attack occurs at the less-hindered, ethyl-bearing oxygen of the peroxide, the methyl group arising from subsequent fragmentation of the alkoxy radical as discussed below. Furthermore, $CrCH_3^{2+}$ proves to be the sole organochromium(III) species produced upon Cr^{2+} reduction of each of the *tert*-butyl peroxides listed in Table I. Consequently a mechanism involving attack at the oxygen bearing the bulky *tert*-butyl residue is precluded whenever less sterically hindered sites of attack are available. In support of this, the very slowest reaction observed is that between Cr^{2+} and di-*tert*-butyl peroxide, $k_1 \leqslant 7.7 \times 10^{-6}$ M^{-1} s^{-1} (23°).

Implicit in the preceding discussion is that "attack" of Cr^{2+} at a *specific* site in the peroxide is a feature of the mechanism, a conclusion made definitive for the ethyl *tert*-butyl peroxide by the observation of the Cr(III) product containing one molecule of coordinated ethanol. That inner sphere attack occurs as a general feature is suggested not only by the low rate for the di-*tert*-butyl peroxide, but by a rate comparison for the reduction of *tert*-butyl hydroperoxide by V^{2+} (1.54 M^{-1} s^{-1})[37] and by Cr^{2+} (1.7×10^4 M^{-1} s^{-1}). Comparison of k_V/k_{Cr} ($\cong 10^{-4}$) with the value expected ($\cong 50$) for outer-sphere electron transfer[38] implies that an inner-sphere mechanism occurs at least in the Cr^{2+}-*t*-BuOOH reaction.

Returning to the specific reaction of ethyl *tert*-butyl peroxide, the experimental results are all in accord with the mechanism shown in reactions 11-13, in which the first-step is rate determining, and the remainder all are fast relative to it.

$$t\text{-}BuOOC_2H_5 + Cr^{2+} \xrightarrow{k_1, H^+} t\text{-}BuO^{\cdot} + Cr(C_2H_5OH)^{3+} \qquad (11)$$



$$t\text{-}BuO\cdot \xrightarrow{fast} CH_3^{\cdot} + (CH_3)_2Co \qquad (12a)$$

$$t\text{-}BuO\cdot \xrightarrow[fast]{Cr^{2+}, H^+} Cr(t\text{-}BuOH)^{3+} \qquad (12b)$$

$$t\text{-}BuO\cdot \xrightarrow[fast]{Cr(H_2O)_6^{2+}} t\text{-}BuOH + (H_2O)_5CrOH^{2+} \xrightarrow[fast]{H^+} Cr(H_2O)_6^{3+} \qquad (12c)$$

$$CH_3 + Cr^{2+} \xrightarrow{fast} CrCH_3^{2+} \qquad (13)$$

The related reaction of *t*-BuOOH, which produces the identical *tert*-butoxy intermediate, shows a 1:2 stoichiometry[10] and gives products easily rationalized[39] according to the chemistry of *t*-BuO . Of importance here is the observation[10] that little ethane is produced (trace amounts only), along with substantial yields of *t*-BuOH (80-94%) and low yields of methane and acetone (18-6%). Reactions subsequent to eq 11 are rapid. The rate constant for unimolecular β-scission of t-BuO· is $k_{12a} \cong 10^3$-10^4 s^{-1} (in CCl_4 at 40°).[40a] Estimates for Cr^{2+}-radical combination, based on known reactions[7] are of the order of $k_{13} \cong 10^7$-10^8 M^{-1} s^{-1}. Evidently reactions 12a and 12b are competitive in rate based on product studies, and nearby every methyl radical produced in eq 12a will subsequently react as in eq 13.

The formation of $CrCH_3^{2+}$ and of the coordinated t-BuOH complex, but not free t-BuOH, establishes that the rapid reactions by which these products are formed, eq 12b and 13, both occur by the inner-sphere mechanism.

In the aqueous solution the nature of the organochromium products is consistent with increased β-scission (eq 14) in the order R = Ph < CH_3 < C_2H_5 ≤ $PhCH_2$, as expected.[41]

$$RC(CH_3)_2O\cdot \rightarrow R\cdot + (CH_3)_2CO \qquad (14)$$

The reaction of n-BuOOH with Cr^{2+} in aqueous solution produces an organochromium cation quite resistant to acidolysis (Tables II and III). Alkoxy radicals containing long side chains are known to undergo rapid intramolecular δ-hydrogen transfer,[40] giving a carbon-centered radical. Such a process is shown for n-BuO· in eq 15, and we propose that the CrR^{2+} product formed in this case is the complex $Cr(CH_2)_4OH^{2+}$ formed by Cr^{2+} reaction with the product of reaction 15. The alternative decomposition of n-BuO· by β-scission to produce formaldehyde and n-C_3H_7·, from which Cr-n-$C_3H_7^{2+}$ would result, is clearly not an important pathway in that the organochromium product observed is by virtue of its reaction rate (Figure 2) clearly different from Cr-n-$C_3H_7^{2+}$ (Table III).

$$CH_3CH_2CH_2CH_2O\cdot \rightarrow \cdot CH_2CH_2CH_2CH_2OH \qquad (15)$$

The formation of $CrCH_2OH^{2+}$ rather than $CrCH_3^{2+}$ when reactions are carried out in the mixed CH_3OH/H_2O solvent requires two additional reactions.

$$t\text{-}BuO\cdot + HCH_2OH \rightarrow t\text{-}BuOH + \cdot CH_2OH \qquad (16)$$

$$\cdot CH_2OH + Cr^{2+} \rightarrow CrCH_2OH^{2+} \qquad (17)$$

Abstractions of H atoms by t-BuO· are generally rapid ($k_{16} \cong 10^4$ M^{-1} s^{-1}),[42] and the rate of eq 17 is known independently:[7a] $k_{17} \cong 1.6 \times 10^8$ M^{-1} s^{-1}. These data are consistent with the present observations, but argue against an alternative source of $\cdot CH_2OH$ shown in eq 18

$$CH_3\cdot + HCH_2OH \rightarrow CH_4 + \cdot CH_2OH \qquad (18)$$

for two reasons: in 12.5 M CH_3OH k_{16} is ca. 10^5 s^{-1}, somewhat larger than k_{12a}, and rate constants for H-atom abstractions by methyl radical, such as k_{18}, are generally quite slow, $k_{18} \cong 10^1$-10^2 M^{-1} s^{-1},[43] too slow to compete with the alternative reaction of methyl radicals (eq 13) under the experimental conditions.

The preponderance of $CrCH_2OH^{2+}$ in the reactions conducted in CH_3OH/H_2O solvent suggests that these arguments apply to the other alkoxy and acetoxy radicals (Table II). One notable exception is the reaction of *tert*-amyl hydroperoxide with Cr^{2+}. In this case the radical generated is $C_2H_5C(CH_3)_2O\cdot$, whose subsequent β-scission (eq 19) is probably fast enough (with $k_{19} = 2 \times 10^5$ s^{-1} [40b]) to compete with H-atom abstraction from methanol.

$$C_2H_5C(CH_3)_2O\cdot \rightarrow C_2H_5\cdot + (CH_3)_2CO \qquad (19)$$

In the reaction *sec*-butyl hydroperoxide, preferential, rapid cleavage of the alkoxy radical to form C_2H_5 is expected,[44] and this is consistent with entries 13 and 14 in Table II.

Rates of Cr^{2+}–Peroxide Reactions. The influence of peroxide structure upon the reduction rate constants k_1 constitutes the dominant effect in a number of reactions reported here. We choose to consider the factors responsible for the variations in k_1 values in terms of steric restrictions at three different sites, C_1, C_1', C_2', relative to the O_1 oxygen atom which product studies and rate parameters identify as the atom attacked by Cr^{2+} in the rate-limiting step.

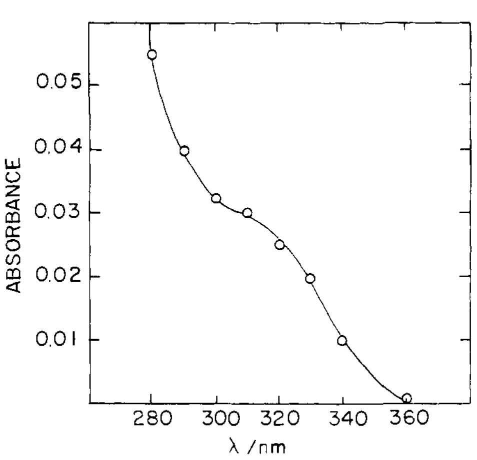


Figure 4. Spectrum of the intermediate observed reaction of Cr^{2+} with perbenzoic acid.

$$C_2'\text{-}C_1'\text{-}O_2\text{-}O_1\text{-}C_1$$

In the series t-BuOOH, $C_2H_5C(CH_3)_2OOH$, cumene hydroperoxide, and $PhC(CH_3)_2OOH$ (entries 4, 5, 6, and 7 in Table I) the -C_2' group varies between CH_3, C_2H_5, C_6H_5, and $C_6H_5CH_2$. Values of 10^{-4} k_1 lie between 0.97 and 2.27 M^{-1} s^{-1}, indicating very little effect of steric crowding by substituents at this remote position upon the rate of attack at -O_1.

In the series t-BuOOH, *sec*-BuOOH, and n-BuOOH (entries 4, 10, and 9) the C_1' group varies from tertiary to secondary to primary, and rate constants vary in a small but systematic manner: $10^{-4}k_1$ = 1.70, 3.60, and 5.83 M^{-1} s^{-1}. These results are indicative of a small steric interference from groups bonded to -O_2, two atoms distant from -O_1.

In the series in which C_1 is varied from H to C_2H_5, -$CH(CH_3)_2$, and -$C(CH_3)_3$ (entries 4, 3, 2, and 1 in Table I), a very marked decrease in k_1 occurs, in all $>10^9$ in this series. This regular and large effect is consistent with direct attack of Cr^{2+} at -O_1 based on steric crowding at the -C_1 position. When -C_1 = C_1' (i.e., for di-*tert*-butyl peroxide), it is no longer possible to conclude that Cr^{2+} attack occurs at oxygen, and this reaction may possibly occur by an outer-sphere mechanism.

In the series of *tert*-butyl perbenzoates[45] studied, there is a mild but systematic variation of $10^{-4}k_1$ (0.82-1.50 M^{-1} s^{-1}) with the Hammett substituent parameter σ (+0.66 to −0.27), resulting in a reaction constant $\rho = -0.28 \pm 0.10$.[46] The overall reaction may be considered in two steps, a preequilibrium between perester and Cr^{2+} (forming a "precursor complex") followed by intramolecular electron transfer to the peroxide. The two steps would appear to have opposing electronic requirements, which nearly cancel, although the former effect may be slightly dominant in view of the small negative value of ρ.[47]

The product of the reaction of *tert*-butyl perbenzoate with Cr^{2+} is the benzoato complex of Cr(III), but the question of the molecular configuration of its transition state remains open. Kochi[8,10] originally pointed to the analogy between the reactions

$$(NH_3)_5CoX^{2+} + Cr^{2+} \rightarrow CrX^{2+} + (NH_3)_5Co^{II}\cdot \qquad (20)$$

$$t\text{-}BuOX + Cr^{2+} \rightarrow CrX^{2+} + t\text{-}BuO\cdot \qquad (21)$$

an analogy which we believe demonstrates considerable merit. The question of which oxygen atom is attacked in the former reaction for X = carboxylate has never been settled by direct experiment, although indirect but seemingly convincing arguments have been advanced for attack at the carbonyl oxygen.[49] Similarly, we are unable to say whether Cr^{2+} attack on *tert*-butyl perbenzoate, which is definitely an inner-sphere process in view of the formation of $CrO_2CC_6H_5^{2+}$, occurs via carbonyl or peroxidic oxygen.[50]

Values[51] of k_1 for Cr^{2+} + benzoyl peroxide (50 M^{-1} s^{-1}) and valeryl peroxide (1.3)[10] are both considerably smaller than the specific rates for *tert*-butyl perbenzoate (1.2×10^4) and perbenzoic acid (3×10^6). In the latter case attack occurs at a completely different site, the OH oxygen, and the rates are not directly comparable. For the other three, both steric and electronic effects complicate the reactivity pattern; ignoring the former, the effect of symmetrical electron-withdrawing groups at *both* oxygen atoms can but induce positive charge in each oxygen,[52] and once again the preequilibrium (precursor complex) term appears dominant.

Perbenzoic Acid and Cr(II) and the Search for $CrC_6H_5^{2+}$. Reaction of Cr^{2+} with perbenzoic acid occurs rapidly, $10^{-6}k_1 = 3 \pm 1$ M^{-1} s^{-1}, some 10^2-fold faster than the H_2O_2 reaction.[3,34] The two reactions presumably afford similar steric constraints in that attack of Cr^{2+} occurs at OH in both cases. The increased reactivity of the former is presumably due to its greater oxidizing strength.

The product of reaction in CH_3OH/H_2O solvent is $CrCH_2OH^{2+}$, the origin of which appears to us to arise from reaction of the benzoyloxy radical with methanol (eq 22), which under these conditions would be expected to compete favorably with decarboxylation (eq 23).[53]

$$C_6H_5CO_2\cdot + HCH_2OH \rightarrow C_6H_5CO_2H + \cdot CH_2OH \qquad (22)$$

$$C_6H_5CO_2\cdot \rightarrow C_6H_5\cdot + CO_2 \qquad (23)$$

The observation of a transient intermediate (Table III, Figures 3 and 4) in the strictly aqueous solvent suggested to us the occurrence of decarboxylation (eq 23) followed by recombination of phenyl radical and Cr^{2+} (eq 24), a process well known to be very rapid for other radicals.[7]

$$C_6H_5\cdot + Cr^{2+} \rightarrow CrC_6H_5^{2+} \qquad (24)$$

The mass spectra of product solutions give evidence for only benzene and carbon dioxide, which is consistent with our identification of the transient as $CrC_6H_5^{2+}$, presuming the latter reacts with H_2O and H_3O^+ as the other compounds do (eq 7).

The available data do not constitute definitive evidence that the observed transient is $CrC_6H_5^{2+}$, but this formulation is consistent with known reactions of the radical intermediates.[55] The phenylchromium cation represents a new and interesting addition to the series of known $(H_2O)_5CrR^{2+}$ complexes[7,11] being the first and only aryl. Its acidolysis is orders of magnitude faster than the other derivatives (ref 7b and Table III), perhaps reflecting the bond strength of Cr-C compared to that of H-C in benzene.

Acknowledgments. We are grateful to the Undergraduate Summer Trainees in the Ames Laboratory who contributed data useful here, Messrs. M. J. Haasl, T. J. McNeese, and J. B. Raff, to Mr. G. D. Flesch of the Ames Laboratory for mass spectral determinations, and to Dr. K. U. Ingold for a helpful discussion of the chemistry of organic free radicals. One of us (M.R.H.) wishes to acknowledge a Senior Fulbright-Hays travel award. Helpful collaborative discussion with Dr. M. D. Johnson under support of a NATO Research Grant is gratefully acknowledged.

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(22) Molar absorptivities of alkylchromium(III) complexes are typically ~200 M^{-1} cm^{-1} at 390 nm.[6,7,11] Other reactions of the alkoxy radical such as eq 12b and 12c are responsible for the yields of CrR^{2+} being lower than theoretical, the Cr(III) products so formed being a *tert*-butyl alcohol complex (12b) or the hexaaquochromium(III) ion (12c). The relative proportion of the latter products was not determined.

(23) The decomposition rates were determined in solutions containing 0–50% CH_3OH, and the rate is largely independent of the methanol content. The implications are that the rate constant is nearly solvent independent in this range and that mixed alcohol–water complexes $(H_2O)_{5-X}(CH_3OH)_X CrR^{2+}$ undergo acidolysis nearly independent of X. Some of the scatter in the data in Figure 2 may reflect the approximate nature of this treatment.

(24) Since the spectra of most alkylchromium species are rather similar, particularly around λ 390 nm, the spectrum itself is insufficient to distinguish between (say) $CrCH_3^{2+}$ and $CrCH_2OH^{2+}$. At lower wavelengths λ 250–290 nm the presence of other absorbing species often masks the more definitive absorbance maxima of RCr^{2+}, thus necessitating ion-exchange separation of products in these cases. In certain instances, for example, $C_6H_5CH_2Cr^{2+}$ λ_{max} 355 nm, ion-exchange is not necessary.

(25) For $CrCH_2OH^{2+}$, ϵ is given as 570 M^{-1} cm^{-1} at 390 nm.[7b]

(26) For $CrCH_3^{2+}$, λ_{max}/nm (ϵ/M^{-1} cm^{-1}) are: 392 (240) and 258 (2520).[11b]

(27) In this situation the simultaneous formation of a *tert*-butyl alcohol complex undoubtedly occurs (from the reaction of *t*-BuO· with Cr^{2+}, however, not from an alternative mode of attack of Cr^{2+} on the peroxide, a point readily seen from the kinetic data of Table I). The tertiary alcohol will not, of course, respond to the oxidation procedure used for analysis of coordinated C_2H_5OH.

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(31) We note without explanation that the peroxide reaction product appears to decompose rather more rapidly than the authentic sample. The solubility of the perbenzoate in aqueous solution is much lower than the concentration cited, however, and reaction with Cr^{2+} was not homogeneous.

(32) The approximate absorption spectrum was obtained by monitoring the absorbance decrease accompanying acidolysis. With $[PhC(O)OOH] = 5 \times 10^{-4}$ M, $[Cr^{2+}] = 1 \times 10^{-3}$ M, $[H^+] = 2 \times 10^{-3}$ M, and $\mu = 1.0$ M, the initial Cr^{2+} reduction is complete within the 4 ms mixing time, whereas acidolysis of $CrC_6H_5^{2+}$ requires ca. 1 s at this $[H^+]$. Extrapolation to zero time and subtraction of the final absorbance gives the desired spectrum.

(33) We are grateful to Mr. G. D. Flesch for the mass spectra determinations.

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$$C_6H_5\cdot + HCH_2OH \rightarrow C_6H_6 + \cdot CH_2OH \qquad (23a)$$

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The Molybdenum–Molybdenum Triple Bond. 1. Hexakis(dimethylamido)dimolybdenum and Some Homologues: Preparation, Structure, and Properties

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Abstract: $Mo_2(NR_2)_6$, where $NR_2 = NMe_2$, NMeEt, and NEt_2, have been prepared from metathetic reactions involving molybdenum halides and the appropriate lithium dialkylamide, and have been characterized by a number of physical techniques. The molecular structure of $Mo_2(NMe_2)_6$ has been determined by single-crystal x-ray diffraction. The space group is $P2_1/c$ with $a = 11.461$ (3) Å, $b = 12.052$ (4) Å, $c = 15.409$ (3) Å, $\beta = 101.83$ (2)°, $V = 2083.3$ (10) Å^3, and $Z = 4$. The molecules lie on centers of inversion and form two crystallographically independent pairs. The two molecules are essentially identical, each having virtual S_6 symmetry; the central Mo_2N_6 skeleton has virtual D_{3d} symmetry, i.e., ethane-like geometry. The Mo–Mo distances are 2.211 (2) and 2.217 (2) Å. The following mean distances and angles were found: Mo–N, 1.98 Å; N–C, 1.47 Å; Mo–Mo–N, 103.7°. The bonds to N are essentially coplanar. The structure has been refined to $R_1 = 0.057$ and $R_2 = 0.075$ using 1897 reflections having $I > 3\sigma(I)$. The short Mo–Mo distance together with other structural and physicochemical properties establish the presence of a Mo–Mo triple bond. The orientations of the planar $MoNC_2$ units lead to six proximal and six distal methyl groups with respect to the Mo–Mo bond. Variable temperature ^1H NMR studies show that proximal and distal methyl groups are frozen out in solution below −30°; at higher temperatures they interconvert rapidly on the NMR time scale. A large chemical shift separation, ca. 2 ppm, between proximal and distal methyl proton resonances reflects the marked diamagnetic anisotropy of the Mo–Mo triple bond. $Mo_2(NMeEt)_6$ and $Mo_2(NEt_2)_6$ show similar ^1H NMR spectra: $Mo_2(NMeEt)_6$ exists in an equilibrium of isomers favoring proximal methyl and distal ethyl groups. No single Raman active band can be assigned to a totally symmetric Mo–Mo stretching vibration due apparently to extensive coupling between this and other vibrational modes. The bonding and structural properties of $Mo_2(NR_2)_6$ are compared with previously reported alkyls, Mo_2R_6, and with related chromium(III) alkyls, dialkylamides, and alkoxides.

The element molybdenum has already been found to be a prolific former of homonuclear metal-metal bonds, especially quadruple ones.[2] A distinct capacity to form triple bonds has also become evident, somewhat more recently. The first triple bond was found[3] in $Mo_2(CH_2SiMe_3)_6$, where the bond length was found to be 2.167 Å and the second[4] in $Mo_2(NMe_2)_6$ where the bond length is 2.214 (2) Å. Most recently, the compound $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2$ has been shown[5] to have a (presumably) triple bond with a length of 2.448 (1) Å, that is, about 0.25 Å longer than in the other two cases.[6]

In the meantime, in our laboratories several compounds containing tungsten-tungsten triple bonds have been prepared and characterized.[7] In this and the two following papers[8,9] we shall describe the preparation, structures, and certain other properties of these new molybdenum and tungsten compounds in detail. Preliminary reports on $Mo_2(NMe_2)_6$ have appeared.[4,10]

Results and Discussion

Synthesis. Analysis of the crude brown product obtained from petroleum extraction of the reaction between $MoCl_5$ and $LiNR_2$ (5 equiv) indicated[11] molybdenum to nitrogen ratios of ca. 1:3.2 and showed valencies of molybdenum somewhat greater than 3. The monomeric compounds $Mo(NR_2)_4$ were then obtained by sublimation at 60–90° ($Mo(NMe_2)_4$) and 80–110° ($Mo(NEt_2)_4$) at 10^{-4} cmHg. Analysis of the residue after sublimation gave molybdenum to nitrogen ratios of ca. 1:2.6 and suggested valencies of molybdenum less than 3. This situation was reminiscent of the behavior of many of the dialkylamides of titanium(III), vanadium(III), and chromi-