completely in agreement with the proposed structures. No change in properties could be detected after treatment with silver nitrate.

The value of K_D was determined largely by the procedure of Wilcox and Gaal.[1d] Olefin was dissolved in 2.00 ml of carbon tetrachloride and shaken with 100.0 ml of 1.0 *M* potassium nitrate at 0.3° for 1 hr. The layers were separated in a separatory funnel and the aqueous layer was centrifuged and then filtered through a Whatman No. 5 filter paper. A 90.00-ml aliquot of aqueous solution was cooled in an ice bath and extracted with 2.00 ml of ice-cold pentane. The pentane solution was then evaluated by gas chromatography on a 10-ft (0.25-in. o.d.) column of 10% UCC-W-982 Silicone on Chromosorb W (60–80). The values for **4** and **5** were greater than five times the value for **3**. However, we do not feel that a reliable estimate could be made for the absolute value of K_D. The extremely high value of K_D for **4** and **5** leads to a high susceptibility to error due to traces of impurities and through incomplete separation of the phases. We obtained variations in the results for these two compounds which we attribute to these factors.

Registry No.—**1**, 498-66-8; **2**, 10466-50-9; **3**, 2826-19-9; **4**, 15914-93-9; **5**, 15914-93-9; silver ion, 14701-21-4.

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Autoxidation of Cyclohexene with *tert*-Butyl Hydroperoxide and Chromium(III) Acetylacetonate

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The system chromium(III) acetylacetonate-*tert*-butyl hydroperoxide has been used to initiate autoxidation of cyclohexene in 1-chlorooctane solvent in the temperature range 30–60°. Oxygen absorption rates and peroxide decomposition rates are presented and contrasted to a similar study of 1-octene. Disappearance rates of chromium(III) acetylacetonate could not be determined spectrophotometrically because of the rapid appearance of an interfering absorption.

In connection with a study of the effectiveness of chromium(III) acetylacetonate and *tert*-butyl hydroperoxide as a free-radical initiator system,[2] an investigation of the autoxidation of cyclohexene initiated by this system has been undertaken. Some kinetic data for the autoxidation and for *tert*-butyl hydroperoxide decomposition in the temperature range 30–60° are presented and compared to that reported earlier for 1-octene.[2]

Experimental Section

Chemicals.—Eastman "White Label" cyclohexene was distilled under nitrogen prior to use. Samples of autoxidized cyclohexene were prepared by bubbling oxygen through cyclohexene (neat) at 30° in the presence of azobisisobutyronitrile for 3 days and analyzed[3] for peroxide content (2.9×10^{-2} *M*). No attempt was made to purify the peroxide formed. Aliquots of this autoxidized cyclohexene were added to solutions of pure cyclohexene in chlorooctane prior to chromium(III) acetylacetonate-*tert*-butyl hydroperoxide initiated autoxidation. All other chemicals have been described previously.[4]

Kinetics.—All kinetic measurements have been described previously.[4] Attempts to study chromium(III) acetylacetonate disappearance rates spectrophotometrically[2] were foiled by the rapid appearance of an absorption of unknown origin in the 336-mμ region. No absorption peak was observed in the 438–440-mμ region [Cr(VI)] during the course of this work, although at higher initial concentrations (~10^{-3} *M*) of chromium(III) acetylacetonate, Cr(VI) was detected in reaction mixtures.

Products.—Products were identified by comparison with gas chromatographic retention times of previously analyzed reaction mixtures[5] or with authentic samples of known reaction products. Analyses were performed on a Perkin-Elmer Model 154D gas chromatograph using a 6-ft stainless steel column packed with silicone grease on "GC-20" (Perkin-Elmer column type O). Helium flow was 8.0 psi, column temperature 148°. Gas chromatograph analyses were performed on three reaction mixtures: one cyclohexene sample was autoxidized by chromium(III) acetylacetonate-*tert*-butyl hydroperoxide at 50°; one cyclohexene sample was autoxidized by azobisisobutyronitrile at 50° similar to the procedure of Mayo, *et al.*;[5] one cyclohexene sample was permitted to react at 50° in the presence of chromium(III) acetylacetonate-*tert*-butyl hydroperoxide *in vacuo*.

Results and Discussion

Tables I and II present initial oxygen absorption rates and *tert*-butyl hydroperoxide decomposition rates

TABLE I

CYCLOHEXENE AUTOXIDATION[a,b] RATES IN THE PRESENCE OF CHROMIUM(III) ACETYLACETONATE AND *tert*-BUTYL HYDROPEROXIDE

$[Cr(acac)_3]_0$ × 10^5 *M*	[*tert*-BuOOH]$_0$, *M*	[Cyclohexene]$_0$, *M*	Rate × 10^6 *M* sec^{-1} 30°	40°	50°
0.00	0.00	4.95	0.0	0.0	0.0
0.00	0.99	4.95	5.26	28.9	56.3
1.35	0.99	4.95	6.76	n[c]	n
2.69	0.00	4.95	0.0	n	n
2.69	0.50	4.95	6.80	n	n
2.69	0.99	0.99	1.29	n	n
2.69	0.99	1.98	3.76	n	n
2.69	0.99	4.95	9.05	n	n
2.69	2.97	4.95	13.5	n	n
2.69	3.96	4.95	14.5	n	n
3.92	0.99	4.95	10.0	17.9	29.2
5.38	0.99	4.95	11.2	n	n
6.10	0.99	4.95	6.66	n	n
7.83	0.50	4.95	n	22.9	25.3
7.83	0.99	1.98	n	21.4	51.9
7.83	0.99	4.95	3.91	35.4, 28.0,[d] 5.50[e]	46.9
7.97	0.00	4.95	0.0	n	n
15.66	0.99	4.95	5.95	28.2	46.8

[a] 1-Chlorooctane solvent. [b] Oxygen pressure = 1 atm. [c] n = no data. [d] Autoxidized cyclohexene added. [e] 1.0×10^{-2} *M* cyclohexenone added.

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[1] Brooklyn College of Pharmacy, Long Island University.

[2] N. Indictor, T. Jochsberger, and D. Kurnit, *J. Org. Chem.*, **34**, 2855 (1969).

[3] W. F. Brill and N. Indictor, *ibid.*, **29**, 710 (1964).

[4] N. Indictor and T. Jochsberger, *ibid.*, **31**, 4271 (1966).

[5] D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Amer. Chem. Soc.*, **87**, 4824 (1965).

TABLE II

tert-BUTYL HYDROPEROXIDE DECOMPOSITION[a,b] RATES IN THE PRESENCE OF CHROMIUM(III) ACETYLACETONATE AND CYCLOHEXENE

$[Cr(acac)_3]_0$, × 10^5 *M*	[*tert*-BuOOH]$_0$, *M*	[Cyclohexene]$_0$, *M*	Rate × 10^7 *M* sec^{-1} 40°	50°	61°
0.00	0.99	1.98	0.34	0.44	n[c]
3.05	0.99	1.98	0.667	3.74	n
3.92	0.99	1.98	n	4.62	7.70
6.10	0.99	1.98	2.27[d]	10.2	n
7.83	0.50	1.98	2.45	9.40	12.4
7.83	0.99	0.00	n	11.1	52.6
7.83	0.99	1.98	4.88	12.8	33.6
7.83	0.99	4.95	4.42	13.0	33.4

[a] 1-Chlorooctane solvent. [b] *In vacuo.* [c] n = no data. [d] Reaction temperature = 30°.

TABLE III

COMPARISON OF *tert*-BUTYL HYDROPEROXIDE DECOMPOSITION RATES AND OLEFIN AUTOXIDATION RATES IN THE PRESENCE OF CHROMIUM(III) ACETYLACETONATE

Temp, °C	$[Cr(acac)_3]_0$ × 10^5 *M*	[*tert*-BuOOH]$_0$, *M*	[Olefin]$_0$, *M*	R_0[a] CHE[c]	Oct[d]	R_p[b] CHE[c]	Oct[d]
30	0.00	0.8	5.0–6.0	5.26	0.0		0.0
30	8.0	0.0	3.0–5.0	0.0	0.17		
30	8.0	0.8	5.0–6.0	3.91	0.53		
30	6.1–9.0	0.8–1.0	2.0–3.0			0.227	25.7
40	6.0–8.0	0.8–1.0	2.0–3.0	21.4	1.15	0.488	56.5
50	6.0–8.0	0.8–1.0	2.0–3.0			1.28	224

[a] R_0 = rate of autoxidation × 10^6 *M* sec^{-1}. [b] R_p = rate of *tert*-BuOOH decomposition × 10^6 *M* sec^{-1}. [c] Cyclohexene data from this work. [d] 1-Octene data from ref 2 and 4.

TABLE IV

EFFECT OF VARIOUS INITIATORS ON THE RELATIVE AUTOXIDATION RATES OF CYCLOHEXENE AND 1-OCTENE

Temp, °C	Initiator	R_{CHE}/R_{Oct}[a]	Ref
80–85	Cobalt propionate	20–30[b]	*c*
60	Azo initiated[d]	13.8[b]	5, *e*
55	Benzoyl peroxide	10.3	*f*
45	Benzoyl peroxide	14.7	*g*
30	Photoinitiated[h]	37	14
40	$Cr(acac)_3$/*tert*-BuOOH	18.6[i]	2, present work
30	$Cr(acac)_3$/*tert*-BuOOH	7.4[i]	2, present work

[a] Estimated on the basis of reported rate constants for propagation and termination. [b] Value for 1-hexene in place of 1-octene. [c] S. J. Moss and H. Steiner, *J. Chem. Soc.*, 2372 (1965). [d] 2,2′-Azobis(2-methylpropionitrile) or 1,1′-azobis(cyclohexane-1-carbonitrile). [e] D. E. Van Sickle, F. R. Mayo, R. M. Arluck, and M. G. Syz, *J. Amer. Chem. Soc.*, **89**, 967 (1967). [f] L. Bateman, *Quart. Rev., Chem. Soc.*, **8**, 147 (1954). [g] J. L. Bolland, *Trans. Faraday Soc.*, **46**, 358 (1950). [h] 1,1′-Azobis(cyclohexane-1-carbonitrile) used as photoinitiator. [i] Based on rate of O_2 absorption.

respectively. Tables III and IV contrast kinetic data for 1-octene and cyclohexene obtained under similar conditions.

Autoxidations.—Unlike the 1-octene system[2] the presence of chromium(III) acetylacetonate is apparently not required for cyclohexene autoxidation. However, addition of small amounts of the chelate do enhance the rate under most conditions. Under comparable conditions of chromium(III) acetylacetonate–*tert*-butyl hydroperoxide concentration, cyclohexene autoxidizes 7–19 times faster than 1-octene. Relative cyclohexene–1-octene autoxidation rates using other initiators are compiled in Table IV and are seen to be roughly comparable.

The dependence of the rate on chromium(III) acetylacetonate at low concentrations ($<4 \times 10^{-5}$ *M*) is kinetically first order but is rapidly reduced as the metal concentration increases. Indeed at some concentrations the chelate retards the reaction (Table I). The lowering of kinetic dependence on initiator with increasing concentration has been observed in other systems.[4,6,7]

In this system the inhibitory effect of added chromium(III) acetylacetonate may arise from several sources. The first of these involves a reaction in which nonradical and therefore nonchain-carrying species are produced (eq 1). It should be pointed out that an

$$\mathrm{Cr(III)} + \mathrm{R}\cdot \longrightarrow \mathrm{Cr(III} \pm n) + \mathrm{R}^{\mp n} \qquad (1)$$

increase in the concentration of chromium(III) acetylacetonate does not decrease the rate of *tert*-butyl hydroperoxide decomposition which occurs in part by a chain mechanism.[2,8] However, the chain-carrying radical may be different in the two cases. It has been shown[9,10] that cyclohexene and its derivatives undergo rapid (relative to 1-octene) polar epoxidation with *tert*-butyl hydroperoxide and metal acetylacetonates. The addition of chromium(III) acetylacetonate may therefore deplete the peroxide concentration *via* a nonradical mechanism. Depletion of peroxide both in the presence[9] and absence[3] of added chromium(III) acetylacetonate in epoxide-forming reactions (performed in the absence of oxygen) has accounted for 10–60% of the decomposed peroxide in the formation of the monoring epoxide of 4-vinylcyclohexene. At high enough metal concentrations the decrease in peroxide concentration might reduce the autoxidation rate. Furthermore, since a product of *tert*-butyl hydroperoxide decomposition is molecular oxygen,[11] an increased rate of O_2 production *in situ* would lead to an apparent decrease in the rate of oxygen uptake.[4] However, it should be noted that O_2 evolution was not found to be a significant factor in 1-octene autoxidation.[12]

It is known[6] that products of an autoxidation often

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(6) K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961).

(7) A. E. Woodward and R. B. Mesrobian, *J. Amer. Chem. Soc.*, **75**, 6189 (1953).

(8) N. Indictor, T. Jochsberger, and D. Kurnit, *J. Org. Chem.*, **34**, 2861 (1969).

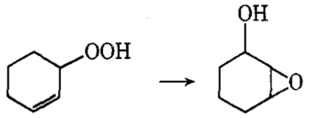
(9) N. Indictor and W. F. Brill, *ibid.*, **30**, 2074 (1965).

(10) M. N. Sheng and J. G. Zajacek, International Oxidation Symposium, San Francisco, Calif., Aug 1967.

(11) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience, New York, N. Y., 1954, p 93.

(12) T. Jochsberger, Ph.D. Thesis, City University of New York, 1968, unpublished results.

inhibit the reaction. During the period of temperature and concentration equilibration of reactants, before kinetic measurements are made, autoxidation products may be built up. Increasing chromium(III) acetylacetonate concentration probably increases product formation and may therefore diminish the reaction rate. Indeed, the respective introduction of small amounts of autoxidized cyclohexene or cyclohexenone, a known product of cyclohexene autoxidation,[5] significantly reduces the autoxidation rate (Table I, *footnotes d* and *e*). The addition of the normally chain-branching cyclohexenyl hydroperoxide in the form of autoxidized cyclohexene might cause depletion of the chromium reactivity by participation in metal-catalyzed rearrangement,[13] by competitive complex formation with the chromuim(III) acetylacetonate, or by producing further decomposition products (such as cyclohexenone) which act as inhibitors. Cyclohexenone may inhibit the reaction by forming phenols or their precursors.



As the concentration of chromium(III) acetylacetonate is increased above a certain value, the inhibitory effect, whatever its source, appears to be overcome and the rate increases. This suggests a higher order initiation process which only becomes important at higher metal concentrations.

The inhibitory effect of chromium(III) acetylacetonate appears to be temperature dependent, increasing in importance with a rise in temperature. At 50° the reaction rate is faster in the absence of metal than in its presence at all concentrations studied. Therefore, whatever the mode of inhibition, it clearly has a higher activation energy than the initiation process.

Unlike the 1-octene system,[2] no reaction occurs in the absence of *tert*-butyl hydroperoxide. The data of Table I indicate that, while the autoxidation rate increases, the apparent kinetic order in peroxide diminishes with increasing peroxide concentration. With 1-octene it was observed that increased *tert*-butyl hydroperoxide–olefin ratios retarded the reaction due to an increase in the concentration of *tert*-butyl peroxy radicals.[12] With cyclohexene this effect is somewhat less dramatic, perhaps due to the more rapid formation of cyclohexenyl compared to octenyl radicals.[14]

The autoxidation rate is kinetically first order with respect to cyclohexene under most conditions. This is again somewhat different from the 1-octene system in which the reaction was first order in olefin only at low concentrations ($<0.3\ M$) and dropped off rapidly with increasing amounts of olefin.[2] This decrease in order is due to an increase in termination *via* unoxidized octenyl radicals. The fact that no decrease is observed with cyclohexene is consistent with the observation that propagation competes more favorably with termination for cyclohexene autoxidation than for 1-octene (eq 2).[14]

$$k_{\text{1-octene}}/k_{\text{cyclohexene}} = 0.027 \qquad (2)$$

where

$$k = k_{\text{propagation}}/(2k_{\text{termination}})^{1/2} \text{ at } 30°$$

As in the case of 1-octene the data indicate that the chromium(III) acetylacetonate–*tert*-butyl hydroperoxide initiated autoxidation of cyclohexene proceeds *via* a multistep mechanism. This leads to a complex kinetic equation of several terms, each one having its own concentration and temperature dependence.

Decomposition of *tert*-Butyl Hydroperoxide.—The rate of *tert*-butyl hydroperoxide decomposition in the absence of metal is consistent with previous work,[8] as is rate enhancement due to the presence of chromium(III) acetylacetonate.[2,4,9] The decomposition of *tert*-butyl hydroperoxide in the presence of metal acetylacetonates may be due to either a radical[2] or nonradical[9,10] process or a combination of both. Although the reaction was observed to proceed almost entirely by a radical-chain mechanism in the presence of 1-octene,[2,8] other olefins apparently undergo a nonradical reaction with the hydroperoxide, especially in the presence of metals,[9,10] to form epoxides.

Tables II and III present *tert*-butyl hydroperoxide decomposition data both in the presence and absence of cyclohexene or 1-octene. It is noted that the presence of cyclohexene retards the decomposition at 61° but has a small accelerating effect at 50°. In the 1-octene system the reverse was observed, *i.e.*, the retarding effect of the olefin diminished with increasing temperature. In the latter case the temperature effect on retardation was attributed to a lower activation energy for the termination process than for hydrogen abstraction. It is known[14] that hydrogen abstraction from cyclohexene is much more facile than from 1-octene, while termination by cyclohexenyl peroxy radicals is some 40 times slower than for octenyl peroxy radicals. It is therefore probable that in the case of cyclohexene the activation energy for termination is not significantly lower than that for propagation. Indeed, from the data of Howard and Ingold[14] and Sajus,[15] the estimated activation energies for propagation and termination in cyclohexene autoxidation are almost identical (~3 kcal/mol).[16] Furthermore, the observation[3,9,10] that cyclohexene and its derivatives interact to a greater extent than 1-octene with *tert*-butyl hydroperoxide in nonradical reactions implies that the two olefins might retard decomposition by different mechanisms.

It is interesting to note that with both cyclohexene and 1-octene there is a relatively large difference in peroxide decomposition rate upon addition of small amounts of olefin. Once the olefin is present the rate is no longer affected by changes in concentration. It was observed in the 1-octene system[2] and in other systems[17-19] that complex formation plays an important role in metal-induced peroxide decompositions. Therefore the whole effect of the olefin might be as a competitive ligand[20-22] for a site on the chromium. The large excess of olefin relative to the metal produces a kinetically "zero" order effect.

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[13] K. Allison, P. Johnson, G. Foster, and M. B. Sparks, *Ind. Eng. Chem. Prod. Res. Develop.*, **5**, 166 (1966).

[14] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **45**, 793 (1967).

[15] L. Sajus, *Advan. Chem. Ser.*, **75**, 59 (1968).

[16] Minimum value of $E_{\text{termination}}$ based on the estimates in ref 15. Some data in this reference lead to higher values.

[17] N. G. Ariko and B. V. Erofeev, *Usp. Khim. Org. Perekisnykh Soedin. Autookisleniya, Dokl. Vses. Konf.*, *3rd*, 354 (1965) (Pub 1969); *Chem. Abstr.*, **72**, 42520m (1970).

[18] W. H. Richardson, *J. Amer. Chem. Soc.*, **87**, 247 (1965).

[19] E. J. Y. Scott, *J. Phys. Chem.*, **74**, 1174 (1970).

[20] P. M. Henry, *J. Amer. Chem. Soc.*, **87**, 990 (1965).

[21] R. Cramer, *ibid.*, **87**, 4717 (1965).

[22] R. J. Cvetanovic, F. J. Duncan, W. E. Falconer, and R. S. Irwin, *ibid.*, **87**, 1827 (1965).

Although autoxidation rates are of the order of ten times faster for cyclohexene relative to 1-octene, the data of Table III indicate that *tert*-butyl hydroperoxide decomposes some hundred times faster in 1-octene than in cyclohexene. It is suggested that this effect is due to the greater ease of hydrogen abstraction from cyclohexene,[14] the greater stability of the cyclohexenyl radical, and the statistical factor (four allylic hydrogen atoms in cyclohexene *vs.* two in 1-octene).

An effort to observe the disappearance of chromium(III) acetylacetonate *via* its ultraviolet absorption peak at 336 mμ[23] was thwarted by the appearance of an absorption of unknown origin at that wavelength. None of the known[5] products of cyclohexene autoxidation were observed to absorb in that region. Since this absorption of unknown origin occurs even in the absence of metal acetylacetonate, it is suggested that the peak arises from a complex between the peroxide and either cyclohexene or product(s). In the 1-octene system[2] the presence of Cr(VI) was detected both chemically and spectrophotometrically; only at higher initial chromium(III) acetylacetonate concentrations ($\sim 10^{-3}$ *M*) than runs reported in this communication was Cr(VI) detected in the cyclohexene system. This implies that the oxidation state of chromium remains essentially unchanged over the course of the reaction[24] probably *via* the usual oxidation–reduction scheme proposed[26] for metal–peroxide reactions (eq 3 and 4). In the

$$\mathrm{Cr(III)} + \mathrm{ROOH} \longrightarrow \mathrm{Cr(IV)} + \mathrm{RO}\cdot + \mathrm{OH}^- \quad (3)$$

$$\mathrm{Cr(IV)} + \mathrm{ROOH} \longrightarrow \mathrm{Cr(III)} + \mathrm{RO_2}\cdot + \mathrm{H}^+ \quad (4)$$

presence of 1-octene a similar scheme was proposed[2] in which, however, Cr(III) does not survive but is oxidized eventually to Cr(VI). Since the Cr(III) disappearance rate is essentially zero in cyclohexene the chain lengths for these reactions must be extremely large based on initiation solely *via* reactions 3 and 4. However, unlike the 1-octene system, the data for cyclohexene autoxidation indicate that an initiation process involving only *tert*-butyl hydroperoxide is also important.

The products detected in cyclohexene autoxidations initiated by chromium(III) acetylacetonate–*tert*-butyl hydroperoxide were the same as those found using azobisisobutyronitrile initiator[5] (cyclohexenone, cyclohexenol, and cyclohexene epoxide) and analyzed under identical gas chromatograph conditions. Results with azobisisobutyronitrile gave good agreement with other product studies[5] made under somewhat different conditions. More ketone was found in the presence of chromium than in the presence of azobisisobutyronitrile; more epoxide was found *in vacuo* than under autoxidation conditions. Although chromium(III) acetylacetonate enhances epoxide formation, the presence of oxygen either causes further reaction of the epoxide or adversely affects complexes that favor epoxide formation.

Registry No.—Cyclohexene, 110-83-8; *tert*-butyl hydroperoxide, 75-91-2; chromium(III) acetylacetonate, 13681-82-8; 1-octene, 111-66-0.

Acknowledgment.—Equipment grants from the City University of New York are gratefully acknowledged.

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[23] R. H. Holm and F. A. Cotton, *J. Amer. Chem. Soc.*, **80**, 5658 (1958).

[24] Although no effort was made to detect other chromium oxidation states (*e.g.*, +2, +4, and +5), these states are known to be unstable relative to the +3 and +6 states (*cf.* ref 25).

[25] J. Kleinberg, Wm. J. Argersinger, Jr., and E. Griswold, "Inorganic Chemistry," D. C. Heath, Boston, Mass., 1960, p 513 ff.

[26] R. Hiatt, K. C. Irwin, and C. W. Gould, *J. Org. Chem.*, **33**, 1430 1968).

Kinetics of Reactions of Amines with Tricarbonyl(fluorobenzene)chromium[1a]

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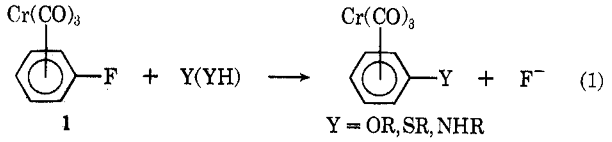
These aminodefluorination reactions occur at convenient rates in dipolar, aprotic solvents. Third-order terms predominate in their rate laws. These terms are first order in substrate, first order in the reacting nucleophilic amine, and first order in a catalytic amine which may or may not be the same as the "reacting" amine. The catalytic effect is taken to be base catalysis, and as an indication that expulsion of fluorine from the intermediate complex is the rate-limiting step, whereas in analogous reactions of *p*-fluoronitrobenzene the initial nucleophilic attack is rate limiting. The data are consistent with the hypothesis that the amine attacks exo to the chromium tricarbonyl moiety and that steric hindrance in the general acid catalyzed expulsion of fluorine from the conjugate base of the intermediate complex is a critical factor.

Chromium tricarbonyl complexes (CTC complexes) of aryl halides undergo nucleophilic replacement of halogen by moieties such as OR, SR, and NR$_2$ much more rapidly than does the parent halobenzene.[2]



A similar effect is found in the p*K*$_a$'s of the CTC complexes of phenol, aniline, and benzoic acid; the acid dissociation constant is considerably increased by complexing. In its effects on p*K*$_a$'s,[2a,3a] on rates of saponification of methyl benzoates,[3b] and on substitution rates with methoxide,[4] the chromium tricarbonyl moiety demonstrates approximately the same electron-attracting effect as the nitro group. However, the activating effects of the nitro group and of the chromium tricarbonyl moiety are not closely correlated. The activating effect of the latter is sometimes greater

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[1] (a) This investigation was supported in part by Public Health Service Research Grant No. GM 14647 from the National Institute of General Medical Sciences; (b) NATO Fellow, 1967–1968, on leave from University of Göttingen, Germany.

[2] (a) B. Nichols and M. C. Whiting, *J. Chem. Soc.*, 551 (1959). (b) M. C. Whiting, U. S. Patent 3,225,071 (1965); *Chem. Abstr.*, **64**, 6694 (1966). (c) U. S. Patent 3,317,522 (1967); *Chem. Abstr.*, **67**, 64543 (1967).

[3] (a) E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen, and W. Semmlinger, *Chem. Ber.*, **91**, 2763 (1958); (b) G. Klopman and F. Calderazzo, *Inorg. Chem.*, **6**, 977 (1967).

[4] D. A. Brown and J. R. Raju, *J. Chem. Soc. A*, 40 (1966).