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Reactions of Superoxide Ion with Hydrocarbons activated by the Tricarbonylchromium Unit

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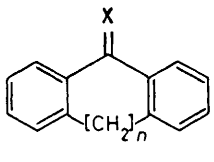
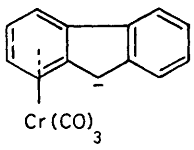
Summary The complexation of a $Cr(CO)_3$ unit to certain aromatic hydrocarbons enhances the benzylic position towards attack by superoxide ion in dimethyl sulphoxide; ketones thus produced are also obtainable by treatment of the corresponding benzylic anion complexes with molecular oxygen.

THE superoxide ion, $O_2^{\bullet -}$, has recently attracted considerable interest because of its demonstrated biochemical ubiquity (all aerobic cells produce it),[1] and as a species of relatively unexplored chemical reactivity.[2] Its ability to function as an oxidising or reducing agent, and also its nucleophilic or basic properties, have made the chemistry of this radical–anion somewhat enigmatic. To help shed some light on the reactivity of $O_2^{\bullet -}$, we have examined several related hydrocarbon substrates in which potential differences in reactivity are controllable by the introduction of π-complexed organometallic species; thus, $O_2^{\bullet -}$ was allowed to react with diphenylmethane and also with its mono- and bis-$Cr(CO)_3$ complexes. The complexation of an arene ring by the $Cr(CO)_3$ unit facilitates, *inter alia*, kinetic generation of a carbanionic site at the α-carbon; the synthetic utility of this effect has already been exploited.[3]



(**1**), $n = 0$, $X = H_2$
(**2**), $n = 0$, $X = O$
(**3**), $n = 2$, $X = H_2$
(**4**), $n = 2$, $X = O$



(**5**)

In a typical experiment, a solution of diphenylmethane–$Cr(CO)_3$ (1·5 mmol) and KO_2 (10 mmol) in dimethyl sulphoxide (DMSO) was stirred at 90 °C for 10 h under N_2. The mixture was poured into ice–water, extracted with ether, and purified by t.l.c. on silica gel yielding 0·16 g (59%) of benzophenone. Other results are presented in Table 1

TABLE 1

Starting material	Oxidised product	% Yield
Ph_2CH_2	$Ph_2C:O$	0
Ph_2CH_2–$Cr(CO)_3$	„	59
Ph_2CH_2-$[Cr(CO)_3]_2$[a]	„	63
(**1**)	(**2**)	0
(**1**)–$Cr(CO)_3$	„	45
(**3**)	(**4**)	30
(**3**)–$Cr(CO)_3$	„	41

[a] Results were not affected by carrying out this reaction under O_2 instead of N_2.

from which it can be seen that (i) in all cases, temporary complexation allows access to the ketone products in reasonable yields, (ii) decomplexation appears to be slow relative to ketone production, yet only non-complexed ketones are isolable, and (iii) monocomplexation is sufficient to activate the ligand but bis-complexation is significantly advantageous since reaction takes place at room temperature. In the case of diphenylmethane ($pK_a = 33{\cdot}4$ according to Streitwieser's scale applicable to the caesium cyclohexylamide–cyclohexyl system)[4], complexation has enhanced the reactivity towards KO_2; for 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (**3**) ($pK_a = 31{\cdot}2$) even the free ligand is active. Fluorene (**1**) ($pK_a = 22{\cdot}7$)[5] is a special case in that, in the presence of KO_2, it exhibits a rapid change in the colour of the solution (from yellow to

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red), but no fluorenone (**2**) was isolated‡ under our standard experimental conditions (*vide supra*).

One may interpret these results by postulating an initial proton transfer from the benzylic position with subsequent attack by molecular oxygen resulting from the disproportionation of $HO_2\cdot$ and $O_2{}^{\cdot-}$ This rapid, highly exothermic, and well established[6] reaction leading to O_2 and $HO_2{}^-$ may well be the driving force for the overall reaction It has recently been suggested that superoxide ion solutions can promote proton transfer from substrates to an extent equivalent to that for the conjugate base of an acid with an approximate pK_a value of 23 (assuming a pK_a of 15 for water) [7] Moreover, it is known that pK_a values of weak carbon acids such as diphenylmethane are 5 5 ± 0·3 pK_a units lower in DMSO than on the Streitwieser scale (28·6 *vs* 34·1) [8] On complexation by $Cr(CO)_3$ the effective acidity of the substrate has increased by a further two or three pK_a units thus bringing it within the superoxide's proton removal capacity

With this hypothesis, the apparent oxidising property of the superoxide ion may be an artefact Thus, the action of $O_2{}^{\cdot-}$ on the ion $[(CO)_3CrPh]_2CH^-$, separately generated and isolated§ as its K^+ salt, gave no rapid formation of ketone in DMSO, in sharp contrast with addition of O_2 to these substrates Thus to confirm that the oxidising properties attributed to the superoxide ion are due to its proton-catalysed conversion into oxygen, we have also studied the reactions of several complexes (see Table 2) with oxygen plus base [9]¶ These reactions, previously explored on non-complexed substrates, are believed[10] to proceed *via* an initial electron transfer [equation (1)]

$$R^- + O_2 \longrightarrow R\cdot + O_2{}^{\cdot-} \qquad (1)$$

TABLE 2

Anion	Product	% Yield
$[PhCr(CO)_3]\text{–}\bar{C}H\text{–}Ph$	$Ph_2C\ \ O$	25
$[PhCr(CO)_3]_2\text{–}\bar{C}H$	$Ph_2C:O$	16
	$Ph_2C:O\text{–}Cr(CO)_3$	22
(**5**)[a]	(**2**)	27
$[PhCr(CO)_3]\bar{C}\text{–}Me_2$	$PhCMe_2OH$	37

[a] In this anion the $Cr(CO)_3$ is known to migrate to the 5-membered ring (K M Nicholas, R C Kerber, and E I Stiefel, *Inorg Chem*, 1971, **10**, 1519

The results in Table 2 strongly support the earlier proposal of an initial proton abstraction by $O_2{}^{\cdot-}$ and subsequent oxidation of the anion thus produced by molecular oxygen arising from the disproportionation of $HO_2\cdot$ All the complexed anions were sensitive to oxygen and the presence of the metal did not diminish the reactivity of the organic ligand

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‡ In a carefully controlled experiment (60 °C, 30 min) a 10% yield of fluorenone (**2**) was isolated from the crude reaction mixture while all the starting material had disappeared

§ The enhanced stabilization provided by the two $Cr(CO)_3$ units allows the isolation and characterization of the anion (n m r spectrum shows $^{13}C\text{-}\alpha$ at 77 4 p p m , d, $^1J_{CH}$ 153 Hz, in $[^2H_8]$tetrahydrofuran)

¶ In a typical experiment, $Ph_2CH_2\text{–}Cr(CO)_3$ (1 5 mmol) and Bu^tOK (5 mmol) were stirred in 15 ml of DMSO for 10 min under N_2 O_2 was bubbled into the flask for 5 min, when the orange solution became dark red After hydrolysis, ether extraction, and t l c purification, benzophenone (70 mg) was isolated No attempts were made to optimise the yields

[1] See for example 'Superoxide and Superoxide Dismutases,' eds A M Michelson, J M McCord, and I Fridovich, Academic Press New York, 1977

[2] For a recent review see E Lee-Ruff, *Chem Soc Rev*, 1977, **6**, 195

[3] For a recent review see G Jaouen in 'Transition Metal Organometallics in Organic Synthesis,' ed H Alper, Academic Press, 1978, vol 2, ch 2

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[6] D Behar, G Czapski, J Rabini, L M Dorfman, and H A Schwarz, *J Phys Chem*, 1970, **74**, 3209

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[8] D J Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, pp 1—45

[9] G A Russell, A G Bemis, E J Geels, E G Janzen, and A J Moye, in 'Oxidation of Organic Compounds,' Am Chem Soc, Washington, 1968, pp 174—202

[10] J G Pacifici, J F Gerst, and E G Janzen, *J Am Chem Soc*, 1965, **87**, 3014, D H R Barton and D W Jones, *J Chem Soc*, 1965, 3563