# Competition Between Base Addition and Electron Transfer in Unsaturated Systems: the Case of 3-Methoxytropone

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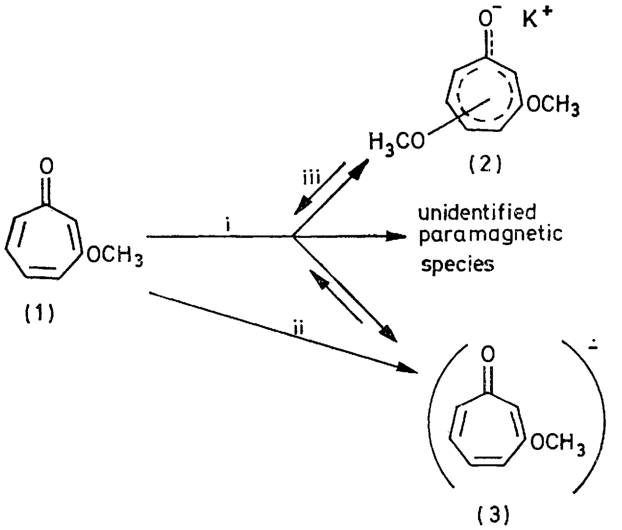
Mixing of 3-methoxytropone with methanolic potassium methoxide in dimethyl sulphoxide leads to a σ-adduct which was observed by u.v. spectroscopy. Also observed was 3-methoxytropone radical anion by both u.v. and e.s.r. spectroscopy. The latter species was also electrolytically generated in both dimethylformamide and dimethyl sulphoxide.

IN the course of studies aimed at the regiospecific functionalization of the cycloheptatrienone nucleus,[1] we have investigated the behaviour of 3-methoxytropone [2] towards potassium methoxide. It is shown here that although there is u.v. evidence for the formation of a σ-adduct [3] between these species, concurrent electron transfer occurs to the polyenone with the formation of unpaired electron species which prevent the observation of the n.m.r. spectrum of the adduct but have an interest *per se*.

*U.v.*, $^1$H *N.m.r., and E.s.r. Studies of the Reaction of* 3-*Methoxytropone with Potassium Methoxide in Dimethyl Sulphoxide.*—To a $10^{-4}$M solution of 3-methoxytropone (1) (Scheme) in dried dimethyl sulphoxide (DMSO), placed in a u.v. spectrophotometric cuvette, was added at room temperature a 5M-methanolic solution of potassium methoxide so as to produce 0.5M-methoxide. Immediately the characteristic absorption of 3-methoxytropone at 280 nm disappeared while a new broad absorption at 335 nm appeared. The same result was obtained at a much higher concentration (0.02M) of 3-methoxytropone using a short-path u.v. cuvette. On neutralization with concentrated hydrogen chloride of the reaction mixture shortly after mixing the reagents, the original spectrum of 3-methoxytropone was immediately restored.



SCHEME i, KOCH$_3$–CH$_3$OH–DMSO; ii, electrochemical reduction in DMF or DMSO; iii, H$^+$

This situation is wholly similar to that encountered with the σ-adduct formed from either 2-methoxy-[4] or 2-chloro-tropone [5] with methoxide, thus suggesting that potassium methoxide adds to 3-methoxytropone at a ring carbon to give a σ-adduct (2) (Scheme). However, in contrast to previous experience,[4,5] detailed structural elucidation by $^1$H n.m.r. spectroscopy of species (2) was not feasible. In fact, using either the

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[1] G. Biggi, F. Del Cima, and F. Pietra, *J. Amer. Chem. Soc.*, 1972, **94**, 4700; 1973, **95**, 7101.

[2] B. Ricciarelli, G. Biggi, R. Cabrino, and F. Pietra, *Synthesis*, 1975, 189.

[3] M. J. Strauss, *Chem. Rev.*, 1970, **70**, 667.

[4] G. Biggi, C. A. Veracini, and F. Pietra, *J.C.S. Chem. Comm.*, 1973, 523.

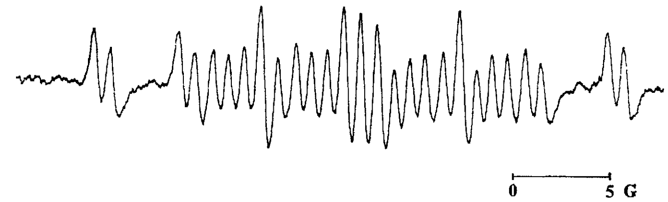
[5] F. Pietra, *J.C.S. Chem. Comm.*, 1974, 544.

continuous wave mode at ordinary n.m.r. reagent concentrations, or with pulsed techniques[5] at low (0.05M), concentrations of both 3-methoxytropone and base no n.m.r. signal was detectable.

Failure to observe n.m.r. signals under such different conditions of reagent concentrations can hardly be attributed to line broadening arising from exchange processes. Therefore, careful re-examination by u.v. spectroscopy of the mixture of 0.02M-3-methoxytropone and potassium methoxide in DMSO at room temperature revealed a slow increase of an absorption at 495 nm suggesting the presence of an unpaired electron species.[6] Therefore, 3-methoxytropone (1) and methanolic 5M-potassium methoxide were mixed in DMSO so as to produce $2 \times 10^{-2}$M-polyenone and 0.37M-base and the mixture was quickly transferred to an e.s.r. tube of *ca.* 2 mm internal diameter. A pattern of e.s.r. signals was, in fact, recorded which, because of lack of symmetry, revealed the presence of at least two paramagnetic species. After *ca.* 20 min those signals which were later identified as arising from 3-methoxytropone radical anion (3) completely disappeared to leave relatively more persistent (*ca.* 1 h) signals due to an unidentified species (Scheme).

*Electrochemical Generation and E.s.r. Studies of 3-Methoxytropone and Tropone Radical Anion.*—On the basis of the above observations, and with the aid of cyclic voltammetry to examine the reduction potential, the radical anion of 3-methoxytropone was electrolytically generated in either DMSO or dimethylformamide (DMF) as solvents with *ca.* 0.1M-tetra-n-butylammonium perchlorate as supporting electrolyte.

The spectra in the two solvents are identical within the limits of experimental accuracy (0.05 G), that in DMSO being shown in the Figure. Assignment of hyperfine splitting constants (h.f.s.c.) was made with the aid of INDO open shell[7] calculations. Assuming a planar, regular heptagon geometry for the seven-membered ring, the experimental values could be satisfactorily reproduced as shown in the Table. The h.f.s.c. fitting was practically independent of the conformation of the methoxy-group, *i.e.* syn- or anti-planar with respect to the carbonyl group.



E.s.r. spectrum of 3-methoxytropone radical union in DMSO

The e.s.r. spectrum of 3-methoxytropone radical anion was also obtained by electroreduction of the mixture of 3-methoxytropone and potassium methoxide in DMSO (see above) after the spectrum of 3-methoxytropone radical anion, which originated on mixing the reagents, had decayed. This poses an interesting question, which we cannot yet fully answer, about the nature of the reducing species.

The ease of obtaining the e.s.r. spectrum of 3-methoxytropone radical anion by electroreduction of 3-methoxytropone in non-basic DMSO contrasts with the reported failure[8] to obtain the spectrum of the radical anion of a related species, tropone, by electroreduction in DMSO. As a matter of fact, however, we could readily obtain the e.s.r. spectrum of tropone radical anion by electrochemical reduction of tropone in DMSO, the spectrum being identical with that reported for reduction in DMF[9] except for the smallest splitting, attributed to 3-H,[9] which could not be detected in our case.

Observed and calculated (INDO) hyperfine splitting constants (G) and calculated (INDO) spin densities for 3-methoxytropone radical anion

| | | Calculated | | | |
|---|---|---|---|---|---|
| | | ($syn$-$OCH_3$) [a] | | ($anti$-$OCH_3$) [a] | |
| Position | Observed h.f.s.c. $a^H$ | h.f.s.c. | Spin density | h.f.s.c. | Spin density |
| 2 | 7.6 | 7.47 | −0.0138 | 7.44 | −0.0138 |
| 4 | 5.9 | 5.01 | −0.0093 | 5.01 | −0.0093 |
| 5 | 4.2 | 4.70 | −0.0087 | 4.68 | −0.0087 |
| 6 | 0.8 | 1.45 | +0.0027 | 1.44 | +0.0027 |
| 7 | 8.5 | 8.90 | −0.0165 | 8.93 | −0.0165 |
| $OCH_3$ | 0.0 | *b* | *b* | *c* | *c* |

[a] With respect to the carbonyl group for a fully planar arrangement. [b] Values of h.f.s.c. between 0.13 and 0.25 G and of spin densities between 0.0005 and −0.0002 were obtained according to the position of methoxy hydrogen atoms with respect to the plane of the seven-membered ring. [c] Values of h.f.s.c. between 0.07 and 0.24 G and of spin densities between 0.0001 and −0.0005 were obtained according to the position of methoxy hydrogen atoms with respect to the plane of the seven-membered ring.

## EXPERIMENTAL

U.v. spectra were taken with either a Unicam SP 800 or a Cary 14 spectrometer. E.s.r. spectra were performed at 9.5 GHz with a home-assembled spectrometer having a sensitivity of *ca.* $5 \times 10^{10}$ spin gauss$^{-1}$ under our working conditions. The radicals were electrochemically generated on a platinum grid directly placed in the cavity within a flat quartz container 0.5 mm deep. The upper portion of the flat cell contained, besides a nitrogen inlet, both a platinum counter electrode and an Ag–AgCl reference electrode which were insulated from the bulk of the solution by means of a glass frit and a bridge of *ca.* 0.1M-tetra-n-butylammonium perchlorate. The lower portion of the flat cell was connected with a reservoir which allowed transfer of the solution for mixing and deoxygenation purposes by means of a nitrogen stream. All experiments were performed at room temperature.

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[6] E. T. Kaiser and L. Kevan, 'Radical Ions,' Interscience, New York, 1968.

[7] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

[8] G. A. Russell and R. L. Blankespoor, *Tetrahedron Letters*, 1971, 4573.

[9] Y. Ikegami, H. Watanabe, and S. Seto, *Bull. Chem. Soc. Japan*, 1972, **45**, 1976.

INDO Calculations[10] were carried out on a 370 IBM computer.

Cyclic voltammetric experiments were carried out under nitrogen at 20°. Both the reference (Ag–AgCl) and counter electrode were insulated from the bulk solution by means of a glass frit and a bridge of 0.1M-tetraethylammonium perchlorate in DMF. A dropping mercury electrode and a hemispherical platinum microelectrode were used.

*Materials*.—Reagent grade DMF was purified according to directions for use in cyclic voltammetry work,[10] except that the solvent was finally collected in Schlenk tubes over activated molecular sieves. Reagent grade DMSO was distilled over calcium hydride at reduced pressure and collected as for DMF. Tropone and 3-methoxytropone (stored as picrate) were available from previous work. Reagent grade tetraethyl- and tetra-n-butylammonium perchlorate were recrystallized according to standard procedures and were dried at 80° under vacuum.

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[10] A. B. Thomas and E. G. Rochow, *J. Amer. Chem. Soc.*, 1957, **79**, 1843.