

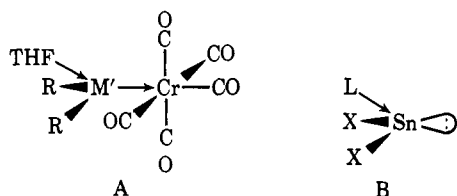
Table I. Spectroscopic Data For $R_2M'Cr(CO)_5 \cdot THF$ Molecules

R_2M'	ν_{CO}^a			$\tau_{CH_3}^b$	$J_{Sn^{117,119}-CH_3}^c$
	$A_1^{(2)}$	$A_1^{(1)}$	E		
$(t-C_4H_9)_2Sn$	2031 (s)	1938 (m)	1918 (s)	8.60	56.0
$(CH_3)_2Sn$	2038 (w)	1941 (m)	1920 (s)	9.20	23.0
$(CH_3)_2Ge$	2043 (w)	1942 (ms)	1922 (s)	9.00	

^a In reciprocal centimeters, m = medium, s = strong, w = weak. Measured in hexane solutions. Band assignments follow ref 13. ^b Measured in toluene- d_8 solutions. ^c In hertz; measured at both 60 and 90 MHz.

120–122° dec. The mass spectrum¹¹ exhibits a parent ion corresponding to $(C_4H_9)_2SnCr(CO)_5^+$.¹²

Our particular structural formulation, A, is well supported by infrared and nmr data (Table I). The solu-



tion infrared spectra are in good accord with an approximately C_{4v} $LCr(CO)_5$ structure¹³ and are, in fact, quite similar to those of the analogous carbene complexes.^{3a} However, the lower frequencies of the C–O stretching vibrations indicate that the divalent germanium and tin ligands are stronger donors of electron density. In fact, the frequencies are qualitatively lower by 10–20 cm^{-1} than for any other neutrally charged $LCr(CO)_5$ molecule yet reported.^{13–15} The positions of the $A_1^{(2)}$ and $A_1^{(1)}$ bands relative to the E mode, which serve as a rough gauge of the π -bonding ability of the group trans to the axial carbonyl,^{13–15} indicate that the new ligands are at least as strong π acceptors as carbenes. Within the series Ia, Ib, Ic, the trend in frequencies is in accord with the trend in electronegativities of the group IV metals and the inductive effects of the alkyl groups.

The pmr spectra are in accord with the proposed formulation of the compounds and are also informative about electronic structure. The small magnitudes of the $J_{Sn^{117,119}-CH_3}$ values indicate that tin is in a low valent state,¹⁶ as would be expected for a stannylene [formally tin(II)] complex. The values are far below the range observed for “normal” tin(IV) transition metal molecules, as for example ones in which a dimethyltin group bridges two transition metals ($J \approx 37$ – 45 Hz).^{16b,c} The nmr also reveals that the coordinated tetrahydrofuran is labile and rapidly exchanges with free tetrahydrofuran in solution at room temperature.

This work demonstrates that transition metal complexes of dialkylgermylenes and -stannylenes can be

(11) Direct inlet spectrum at 80°, 20 eV. We thank Mr. D. A. Netzel for assistance with this measurement.

(12) This ion fragments by progressive loss of CO, which is typical of metal carbonyl compounds, and exhibits the complex multiplet structure expected from the presence of the various chromium and tin isotopes.

(13) L. M. Haines and M. H. B. Stiddard, *Advan. Inorg. Chem. Radiochem.*, **12**, 53 (1969).

(14) The next lowest is for a carbene complex,^{3a} $(CO)_5CrC(OCH_3)_2$ [$p-(CH_3)_2NC_6H_4$] where $A_1^{(2)} = 2054$, $B_1 = 1976$, $A_1^{(1)} = 1943$, and E = 1935 cm^{-1} . We have been unable to observe the weak B_1 mode in our spectra, presumably due to higher local symmetry at the chromium. Traces of $Cr(CO)_6$ present as a decomposition product also interfere.

(15) (a) F. T. Delbeke, E. G. Claeys, and G. P. van der Keln, *J. Organometal. Chem.*, **28**, 391 (1971); (b) W. A. G. Graham, *Inorg. Chem.*, **7**, 315 (1968); (c) F. A. Cotton, *ibid.*, **3**, 702 (1964).

(16) (a) N. Flitcroft and H. D. Kaesz, *J. Amer. Chem. Soc.*, **85**, 1377 (1963); (b) H. R. Patil and W. A. G. Graham, *ibid.*, **87**, 673 (1965); (c) D. E. Fenton and J. J. Zukerman, *ibid.*, **90**, 6226 (1968).

prepared, and these have properties distinctly different from the analogous carbene complexes and complexes of tetravalent germanium and tin. The divalent metals appear to function simultaneously as Lewis acids (to tetrahydrofuran) and strong Lewis bases (to chromium). This behavior is consistent with the structural chemistry of a number of tin(II) halides, B, in which the tin coordinates to a base (*e.g.*, H_2O) and is proposed to also possess a “stereochemically active” lone pair.¹⁷ The chemistry of the divalent group IV metal–transition metal compounds and related species is under continuing investigation.¹⁸

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(17) R. E. Rundle and D. H. Olson, *Inorg. Chem.*, **3**, 596 (1964).

(18) (a) T. J. Marks and A. M. Seyam, *J. Organometal. Chem.*, **31**, C62 (1971); (b) T. J. Marks, manuscript in preparation.

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Alternating Line-Width Effects in the Electron Spin Resonance Spectra of 2-Cyclohexenone Radical Anion and Its Simple Alkyl Derivatives

Sir:

Several recent reports exist of the electron spin resonance (esr) spectra of the radical anions of α,β -unsaturated ketones.^{1–4} In particular, Russell and Stevenson,¹ by means of electrolytic reduction in dimethylformamide, have prepared and characterized the ketyls of several 2-cyclopentenones and 2-cyclohexenones in which all hydrogen atoms in positions α to the π system are substituted by methyl groups. They have also demonstrated that the reported esr spectrum of 4,4-dimethylcyclohexenone radical anion of Chen and Bersohn² is due to a semidione. A few examples of straight-chain ketyl radicals have been published by House, *et al.*,³ and Harbour and Guzzo,⁴ but in these cases, as with those of Russell and Stevenson,¹ observation of the often transient radical anion depends critically on substitution of key positions with blocking groups such as methyl, *tert*-butyl, or a cyclo-

(1) G. A. Russell and G. R. Stevenson, *J. Amer. Chem. Soc.*, **93**, 2432 (1971).

(2) H.-L. J. Chen and M. Bersohn, *Mol. Phys.*, **13**, 573 (1967).

(3) K. W. Bowers, R. W. Giese, J. Grimshaw, H. O. House, N. H. Kolodny, K. Kronberger, and D. K. Roe, *J. Amer. Chem. Soc.*, **92**, 2783 (1970).

(4) J. Harbour and A. V. Guzzo, *Mol. Phys.*, **20**, 565 (1971).

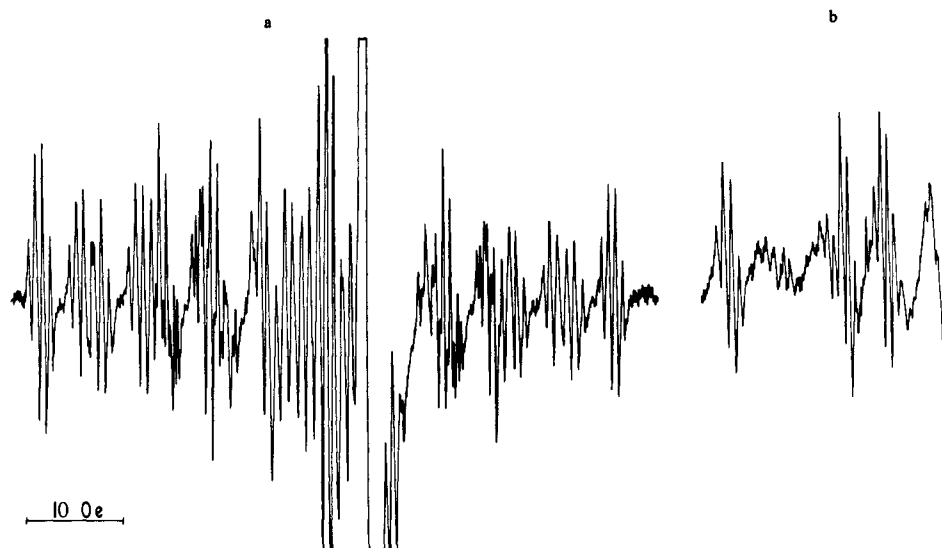


Figure 1. ESR spectra of 2-cyclohexenone radical anion in liquid ammonia (a) at 208°K, (b) at 229°K.

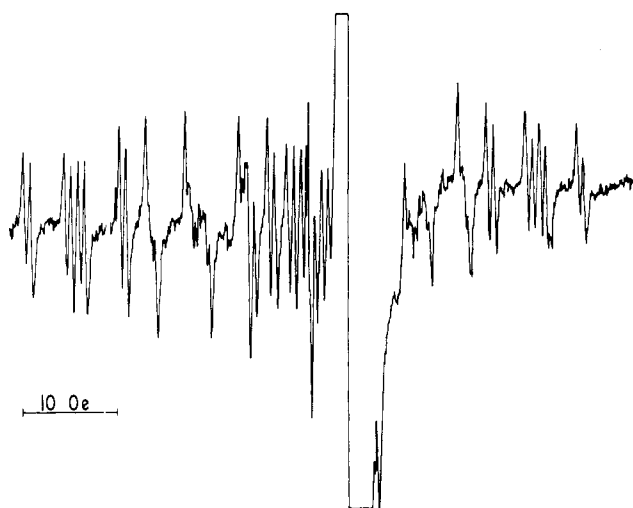


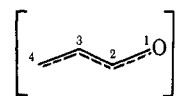
Figure 2. ESR spectrum of 5,5-dimethylcyclohexenone radical anion in liquid ammonia at 200°K.

hexyl or cyclohexenyl system, and in the absence of such groups reduction yields undetectably low radical concentrations.¹

trometer, dilute solutions in liquid ammonia of organic solute and of sodium, and introducing in addition a temperature-controlled cryostat through which the solutions could be forced before mixing. Variation of the conditions of refrigeration enabled the temperature dependences of the resulting spectra to be ascertained.

The success of this approach can be gauged from the ESR spectra obtained from 2-cyclohexenone at 208 and 229°K, given in Figure 1, and from 5,5-dimethylcyclohexenone at 200°K, given in Figure 2. Spectra of comparable resolution were obtained from ketyls of several di- and trimethyl-substituted 2-cyclohexenones (Table I) and also the open-chain mesityl oxide (see below).

Assignment of coupling constants for the 2-cyclohexenones was achieved by a combination of systematic substitution of the various protons by methyl groups and simple Hückel molecular orbital (HMO) calculations. For the fragment



the calculations predict the highest spin density to be

Table I. Hyperfine Coupling Constants (Oersteds) for Ketyls of 2-Cyclohexenones

Cyclohexenone	Temp, °K	a_2	a_3	a_{4a}	a_{4e}	a_{5a}	a_{5e}	a_{6a}	a_{6e}	g factor
Unsubstituted	208	0.78	13.29	23.52	6.14 ^a	0.78	0.78	12.92	4.35 ^a	2.0037
3,5-Dimethyl	203	1.25	14.81 ^b	23.19	7.46	0.74		13.81	4.62	2.0037
4,4-Dimethyl	208	<1	~13.0	<1 ^b	<1 ^b	<1	<1	~13.0	~4.8	2.0036
5,5-Dimethyl	200	0.72	13.20 ^a	23.70	5.8			12.90 ^a	4.38	2.0037
4,4,6-Trimethyl	208	<1	~12.9	<1 ^b	<1 ^b	<1	<1	~12.9	<1 ^b	2.0037
3,5,5-Trimethyl	~230	1.20	14.29 ^b	22.55	6.89			13.66	4.35	2.0037

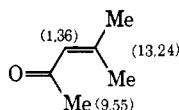
^a Exhibiting line broadening. ^b Methyl proton coupling constant.

It seemed of interest to us, therefore, to attempt the preparation of the ketyl radicals of simple, unsubstituted α,β -unsaturated ketones by means of the low-temperature continuous-flow method described previously⁵ for mixing, in the resonant cavity of the spec-

on positions 2 and 4 ($4 > 2$) and the lowest spin density on position 3. This is substantiated by the unequivocal

(5) A. R. Buick, T. J. Kemp, G. T. Neal, and T. J. Stone, *J. Chem. Soc. A*, 666 (1969).

assignment of the couplings found for the mesityl oxide radical anion, *viz.*



Assignment of the coupling constants of the C_4 and C_6 methylene protons in the 2-cyclohexenone system has been made assuming pure axial and equatorial conformations for these protons and proportionality between the spin density on these centers and (a) the spin density on the contiguous carbon atom of the π system and (b) $\cos^2 \theta$, where θ is the dihedral angle between the plane of the methylene C-H bond and the axis of the $2p_z$ orbital of the carbon atom.

Figure 1 illustrates a pronounced alternating line-width effect in the esr spectrum of 2-cyclohexenone, a phenomenon becoming accentuated at higher temperatures. Similar effects were apparent in the spectra of 5,5-dimethylcyclohexenone and 3-methylcyclohexenone. In the parent molecule, time averaging of the C_{5a} and C_{5e} protons is found, and the lines due to C_{4e} and C_{6e} are broadened while those from C_{4a} and C_{6a} remain sharp. This implies that the precession frequencies of the electron moment about the nuclear moments due to the C_{4e} and C_{6e} protons are comparable with the frequency of the associated conformational change. Using an averaged value for the couplings of C_{4e} and C_{6e} protons affords a frequency of 14 MHz, *i.e.*, a conformational lifetime of 7×10^{-8} sec. In 5,5-dimethylcyclohexenone, line broadening is found for the protons in the C_3 (13.20 Oe) and C_{6a} positions (12.90 Oe), leading to a flipping frequency of 3.7 MHz and a conformational lifetime of 3×10^{-8} sec. Although we have not yet completely analyzed the esr spectrum from the ketyl of 3-methylcyclohexenone, the conformational lifetime is similar to that found for 2-cyclohexenone. No line broadening was apparent in the temperature range 203–233°K for the 3,5-dimethylcyclohexenone ketyl.

The microwave spectrum of 2-cyclohexenone⁶ indicates that all the heavy atoms except C_5 are coplanar, and the conformational change affecting the esr spectrum of the anion probably involves movement of C_5 above and below this plane. In the case of 3,5-dimethylcyclohexenone, an axial conformation for the C_5 methyl group is probably preferred.

The general pattern of spin density distribution closely follows those reported by Russell and Stevenson,¹ House, *et al.*,³ and Harbour and Guzzo.⁴ Further details of this work and its extension to a number of other α,β -unsaturated ketones and some unsaturated nitriles will be reported in due course.

Acknowledgment. The Science Research Council and Imperial Chemical Industries, Ltd., are thanked for financial report.

(6) S. A. Manley and J. K. Tyler, *Chem. Commun.*, 382 (1970).

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Direct Observation of Triplet Exciplexes by Flash Photoconductivity and Flash Spectroscopy. Formation of Three-Component Exciplexes between Porphyrins and Nitro Aromatics

Sir:

Exciplex formation has been well documented as a mechanism for deactivation of excited singlet and triplet states for a wide variety of compounds.¹⁻³ Direct examination has been mostly limited to the observation of fluorescence from certain singlet exciplexes in solution and to detection of phosphorescence from certain triplet donor-acceptor pairs activated in hydrocarbon glass at 77°K.⁴ We have previously found indirect chemical evidence for the formation of singlet and triplet exciplexes between excited metalloporphyrins and aromatic nitro compounds.^{5,6} In the present paper we wish to report direct observation and study of triplet exciplexes for these systems both by flash spectroscopy as well as by means of a flash photoconductivity technique. A most interesting and important feature of the triplet exciplexes under investigation is the preferential formation of three-component excited complexes.

The system under investigation consists of degassed benzene solutions with zinc etioporphyrin I as excited donor and *trans-p*-nitrostilbene (PNS) and *p*-nitrotoluene (PNT) as acceptor-quenchers. Flashing of dilute ($5 \times 10^{-5} M$) solutions of porphyrin in the presence of quencher leads to transients absorbing weakly in the range 440–580 nm (λ_{max} 450 nm for zinc etio-PNS and 440 nm for zinc etio-PNT). Flashing the same solutions in a flash photoconductivity apparatus⁷ also leads to production of strong transient signals having lifetimes in the millisecond range. The decay times for these transients were in all cases identical with those of the transients observed by flash spectroscopy.⁸ Dark conductivity, steady-state photoconductivity, and action spectra (wavelength dependence of conductivity) were also measured; both dark and photoconductivity are higher with quencher present than for zinc etioporphyrin I alone. In a typical experiment a *ca.* tenfold increase in conductivity occurred on flashing. The relatively large increase in conductivity on exciplex formation reinforces the assumption that charge-resonance stabilization is dominant for these systems. While the two techniques are complementary, the flash photoconductivity method is simple and convenient and should prove to be of general utility for future studies.

Using both of the above techniques we have measured exciplex⁹ decay times as a function of quencher concen-

(1) B. Stevens, *Advan. Photochem.*, **8**, 161 (1971).

(2) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968), and references therein.

(3) L. M. Stephenson and G. S. Hammond, *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969), and references therein.

(4) H. Beens and A. Weller in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1969, p 203.

(5) I. G. Lopp, R. W. Hendren, P. D. Wildes, and D. G. Whitten, *J. Amer. Chem. Soc.*, **92**, 6440 (1970).

(6) D. G. Whitten, I. G. Lopp, and P. D. Wildes, *ibid.*, **90**, 7196 (1968).

(7) N. Houser and R. C. Jarnagin, *J. Chem. Phys.*, **52**, 1069 (1970).

(8) The porphyrin triplet was detected by flash photoconductivity; however, the signal was much weaker than those for exciplexes.

(9) Identity of the transient as an exciplex rather than a ground-state intermediate is supported by the observation that it is quenched by azulene as well as oxygen. At the lowest [quencher] studied triplet quenching is complete while singlet quenching is unimportant;^{5,6} while exciplex multiplicity has not been determined, spin-conservation considerations suggest it is a triplet.