negative). The derivation of eq 3 will be given elsewhere, but simply assumes that polarized benzyl bromide is formed at a rate proportional to peroxide decomposition and relaxes with a rate constant k_2.[9] In Figure 1, $k_1 = 4 \times 10^{-3}$ sec^{-1}, $k_2 = 1 \times 10^{-1}$ (our measurements), and $\alpha/\beta = -27$, for benzyl bromide.

Similar polarizations are observed in the spectra of benzyl chloride obtained under comparable conditions in the presence of either CCl_3SO_2Cl or *tert*-butyl hypochlorite (together with B in the first case), benzyl iodide, and B in the presence of CCl_3I (except that emission and absorption are now reversed!), and of toluene in the presence of thiophenol or *tert*-butyl mercaptan. The bibenzyl monitor shows that peroxide decomposition rates are similar in all these systems, so that induced decompositions are unimportant.

On the other hand, enhancement factors in the CCl_3Br system are sensitive to both peroxide and CCl_3Br concentration. Further, benzyl bromide produced in the short-chain bromination of toluene by CCl_3Br using *tert*-butyl hyponitrite initiator (5%) is only weakly polarized[10] and benzyl chloride from toluene–*tert*-butyl hypochlorite shows no polarization whatever. Neither was polarization noted in the small amount of benzyl chloride obtained on decomposing phenylacetyl peroxide alone in CCl_4.

Our results show plainly that *the same displacement reaction may give varying yields of polarized species depending upon reaction conditions.*[11] This clearly rules out any mechanism of polarization during the displacement step as has been suggested by Gerhart and Osterman.[12] Since polarization is sensitive to peroxide concentration and polarized products are observed which are not derived from radicals initially produced in pairs (*e.g.*, benzyl bromide and $CHCl_3$ from the CCl_3Br–toluene reaction), a second alternative, *polarization during separation of initial radical pairs, is also eliminated.*[13] The above results, together with the general finding that polarization decreases in chain processes where a low radical concentration still gives rise to reasonable product yields, suggest that the critical variable in our systems is essentially the *total radical flux* and accordingly that *polarization occurs from subsequent near encounters of radical pairs*, which, in any system, maintains a quasi-steady-state concentration of polarized species.[14] *If a thus polarized radical undergoes a displacement (or other) reaction prior to relaxation, polarized products result.*[15] As a consequence, enhancement factors depend upon both radical flux and the relative rates of radical reactions and radical relaxations.

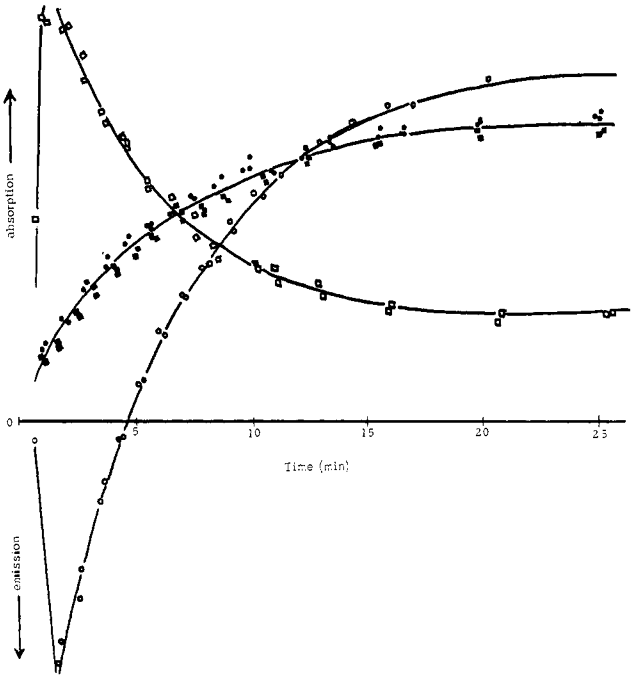

Figure 1. Integrated pmr methylene peak intensity variation with time for $C_6H_5CH_2CH_2C_6H_5$ (■, ●), $C_6H_5CH_2Br$ (○), and $C_6H_5CH_2CCl_3$ (□) from two reactions of 0.11 *M* phenylacetyl peroxide and 0.32 *M* bromotrichloromethane in carbon tetrachloride at 40°.

We have carried out a detailed kinetic analysis of this model which proves to be consistent with our data and yields plausible rate constants for both the polarizing near-approach ($k \sim 10^{10}$ l./mol sec) and subsequent relaxation of the polarized radicals ($k \sim 10^4$ sec^{-1}) and contains no other adjustable parameters. We believe that this is the first direct experimental measurement of a rate constant for the polarization process and details will be reported in our full paper.

Acknowledgment. Support of this work by a grant from the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

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[9] A similar treatment has been given by T. Koenig and W. R. Mabey.[4e]

[10] A strong emission from $CHCl_3$ is also observed. Polarized spectra from $CHCl_3$ are particularly intense due to its slow relaxation.[4e]

[11] The important distinction must be made between the *formation* of polarized species and the actual *observation* of polarized spectra, since the latter depends as well upon the relative rates of radical formation and relaxation of nucleon spins (*cf.* eq 3). However overall half-lives of all reactions reported here were at least as short as the peroxide decompositions.

[12] F. Gerhart and G. Osterman, *Tetrahedron Lett.*, 4705 (1969).

[13] This need not always be the case, and a system involving a displacement reaction in which polarization occurs by this mechanism has recently been reported by G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 7227 (1970). We thank the authors for a copy of their manuscript prior to publication.

[14] If current theories[1,2] are correct these near encounters must be sorting processes in which lone pairs react and others separate. Indeed, our finding of opposite signs of polarization for displacement and coupling products give further support to this interpretation.

[15] We assume that effective benzyl radical polarization requires interaction with unlike radicals, in most of our cases, with $CCl_3\cdot$. Thus in the phenylacetyl peroxide–carbon tetrachloride system the very low reactivity of CCl_4 with benzyl radicals leads to formation of very few $CCl_3\cdot$ radicals and, accordingly, no polarization of the benzyl chloride.

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Singlet Ground State in Tetrabutylammonium Bis(toluene-3,4-dithiolato)cobaltate

Sir:

At high temperatures (77–300°K), tetrabutylammonium bis(toluene-3,4-dithiolato)cobaltate, (n-Bu_4N)[Co(tdt)$_2$], exhibits a magnetic moment of 3.18 BM.[1] Also, measurements on solutions of the compound in various solvents, including pyridine, at room temperature yield moments of 3.33–3.43 BM.[1] From these observations, it was logically concluded that this compound was

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[1] R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Amer. Chem. Soc.*, **88**, 43 (1966).

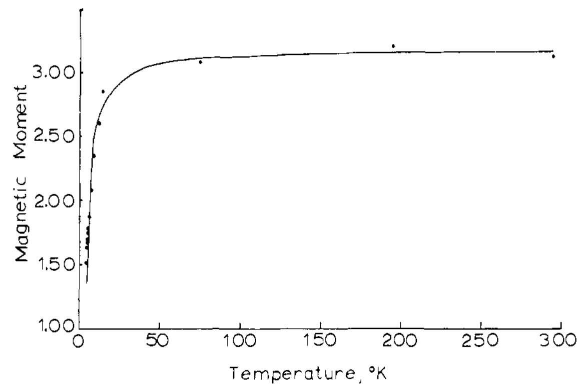

Figure 1. The temperature variation of the observed (●) and the calculated (—) magnetic moments of tetrabutylammonium bis(toluene-3,4-dithiolato)cobaltate.

unique, being the first example of a high-spin square-planar transition metal complex with a triplet ground state. However, the Weiss constant of 14°K reported by Balch, Dance, and Holm[2] is somewhat high for magnetically dilute $^3B_{1g}$ states, and further study on this compound was indicated.

We have extended the magnetic susceptibility measurements to 4.2°K using a Foner-type vibrating sample magnetometer[3] operated at a field strength of 10,000 Oe and calibrated with a sample of very pure nickel metal and with $HgCo(NCS)_4$.[4] Temperature measurements were obtained with a precision germanium resistor and a high-impedance ac resistance bridge. The experimentally determined susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants.[5]

The dramatic feature of the low-temperature magnetic data is a pronounced maximum of the magnetic susceptibility near 8°K. This behavior of the magnetic susceptibility indicates that the ground electronic state is of singlet multiplicity with only a small energy difference existing between this state and the paramagnetic triplet state. The temperature variation of the magnetic moment is shown in Figure 1.

With the assumption that these two electronic states (singlet ground state and low-lying triplet state) are sufficiently separated from other excited states such that the Van Vleck equation (eq 1)[6,7] applies, we have compared the data to the equation and find, from the best fit of experimental and calculated susceptibilities as determined by the minimum least-squares deviation,

$$\chi_m = \frac{2g^2N\beta^2}{3kT}[1 + (1/3)\exp(+\Delta E/kT)]^{-1} \qquad (1)$$

that $\Delta E = 8.5$ cm^{-1}. Thus, while the bis(toluene-3,4-dithiolato)cobaltate ion does not have a triplet ground state, it remains a unique compound, since it is apparently the only known monomeric dithiolato square-planar complex with a singlet ground state and a low-lying triplet state, with configurations of $(\pi_2)^2$ and $(\pi_2)(\pi_1)$, respectively.

Although the structure of $(n\text{-}Bu_4N)[Co(tdt)_2]$ has not been reported, in the triphenylmethylarsonium salt,[8] the cobalt ions are separated by 10.21 Å. This observation, coupled with the absence of the characteristic behavior associated with the supercooling of substances with lattice antiferromagnetism and with the triplet-state electron spin resonance spectrum which was obtained,[9] discounts the possibility of pairwise or longer range ordering of the magnetic ions as explanations for the magnetic properties.

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[3] S. Foner, *Rev. Sci. Instrum.*, 30, 548 (1959).

[4] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

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[9] C. R. Ollis, unpublished work.

[10] NSF Trainee, 1968–1971.

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Photocycloaddition of Arylazirenes with Electron-Deficient Olefins

Sir:

Previous reports on the photoreductive dimerization of acyclic aryl *N*-alkylimines showed that the reaction did not involve the excited state of the imine at all, but was the result of a ground-state reaction of the imine with a ketyl radical.[1,2] The ketyl radical was derived from carbonyl compounds present in starting material as an impurity, an added sensitizer, or as a photogenerated species. The low photoreactivity of the imine chromophore was attributed to facile deactivation of the excited state as a consequence of rotation about the C–N double bond.[1] In rigid systems, this mode of energy dissipation would not be available and these molecules would have maximum opportunity to undergo reaction from an electronically excited state. In this communication we wish to report that the rigid arylazirene system readily undergoes photochemical addition to electron-deficient olefins.

A solution of phenylazirene[3] (**1**) (0.5 g) in excess methyl acrylate (200 ml) was irradiated under a nitrogen atmsophere using an internal water-cooled mercury arc lamp (450 W) equipped with a Vycor filter. The usual work-up and distillation gave the 1:1 adduct, 2-phenyl-4-carbomethoxy-Δ^1-pyrroline (**2a**), in good yield (80%). The spectral data were in accord with the assigned structure:[4] mass *m*/*e* 203 (parent), 144,

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[1] A. Padwa, W. Bergmark, and D. Pashayan, *J. Amer. Chem. Soc.*, **90**, 4458 (1968); **91**, 2653 (1969).

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[3] G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962).

[4] All compounds analyzed satisfactorily. Complete spectroscopic and degradative details will be given in our full publication.