Persistent Cation Radicals containing Carboxamide and Thiophosphinic Amide Functions. The One Electron Oxidation of Acceptor Stabilized 1,4-Dihydropyrazines

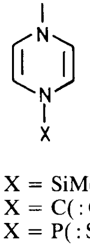
Christian Bessenbacher, Renate Gross, and Wolfgang Kaim*

Institut für Anorganische Chemie, Niederurseler Hang, D-6000 Frankfurt am Main 50, Federal Republic of Germany

Even when it is N,N′-disubstituted by the acceptor groups C(O)Me and P(S)Me$_2$, the 1,4-dihydropyrazine system remains sufficiently electron rich to undergo facile one-electron oxidation to give persistent radical cations with acetamide and thiophosphinic amide functionality.

Stabilization of the cyclic 8π electron system 1,4-dihydropyrazine in the C-unsubstituted form has so far been accomplished by only a few types of N-substituent. The virtually planar[1] trimethylsilyl and trimethylgermyl derivatives (**1**) are coloured, paratropic and highly reactive (pyrophoric),[2] whereas *N*-acylated compounds[3] such as (**2**) display no such unusual behaviour. This dichotomy has raised questions on whether the elusive 1,4-dihydropyrazine may be stabilized by other π accepting N-substituents and to what extent such compounds still retain the typical reactivity of 1,4-dihydropyrazines, *i.e.*, one electron oxidation to give persistent radical cations.[4]

We report here the successful stabilization of the 1,4-dihydropyrazine system by the dimethylthiophosphinyl group, P(S)Me$_2$, which had proved to be a good acceptor for carbon π systems;[5] the colourless, air-sensitive compound (**3**) was obtained *via* reductive thiophosphinylation of pyrazine with Li and ClP(S)Me$_2$. The ^{1}H chemical shift, δ 5.46, for the ring protons in (**3**) is larger than in corresponding trimethyl-silyl and -germyl derivatives (**1**),[2] in agreement with the stronger acceptor effect of the P(S)Me$_2$ group.[5] However, electrochemical studies using cyclic voltammetry in MeCN–0.1 M Bu$_4$NClO$_4$ at 100 mV/s reveal that both (**3**) and the N,N′-diacetyl species (**2**)[3] are still reversibly oxidized at rather low potentials, the second oxidation step to the pyrazinium dication being irreversible in both instances (Figure 1).



(**1**) X = SiMe$_3$ or GeMe$_3$
(**2**) X = C(:O)Me
(**3**) X = P(:S)Me$_2$

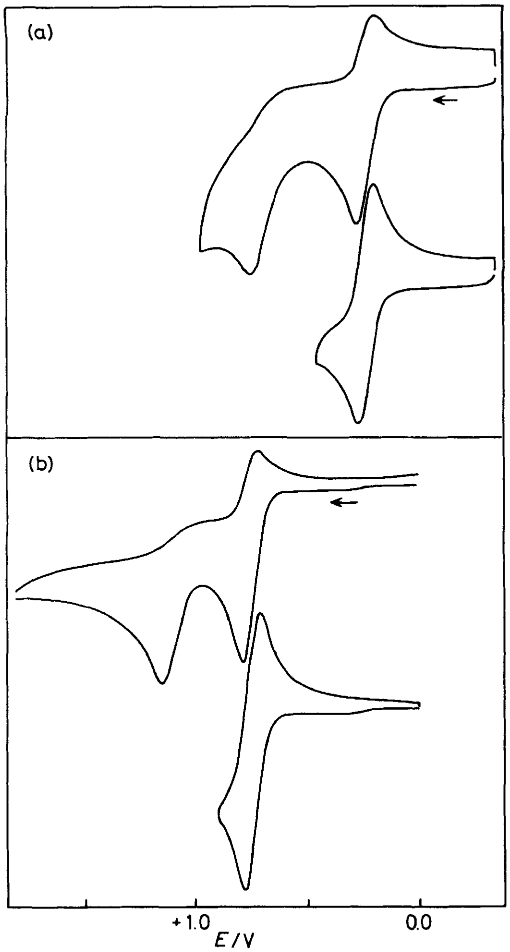


Figure 1. Cyclic voltammograms of (a) compound (**3**) and (b) compound (**2**), illustrating reversible first and irreversible second oxidation steps. Oxidation potentials E_1 +0.26 V for (**3**) and +0.74 V for (**2**); second anodic peak potentials E_2pa +0.79 V for (**3**) and +1.12 V for (**2**) at 100 mV/s scan rate (V *vs.* standard calomel electrode).

The potential differences betwen (**2**) and (**3**) indicate that the stabilization effect of C(O)Me is larger than that of the $P(S)Me_2$ substituent. Encouraged by this reuslt, we characterized the one electron oxidation products, the cation radicals $(\mathbf{2})^{\cdot+}$ and $(\mathbf{3})^{\cdot+}$ by e.s.r. spectroscopy. The e.s.r. parameters of *in situ* electrogenerated $(\mathbf{3})^{\cdot+}$ in MeCN are: g 2.0031, a_N 0.68, a_H (CH) 0.34, a_P = 0.78 mT. The radical cation $(\mathbf{2})^{\cdot+}$ was generated by $AlCl_3$ oxidation[4] in CH_2Cl_2 and has g 2.0027, a_N (av.) 0.58 a_H (CH) (av.) 0.29 mT. Apparently, the e.s.r. spectrum of $(\mathbf{2})^{\cdot+}$ is complicated by the existence of *cis*- and *trans*-isomers as in the isoelectronic 1,4-diacetylbenzene radical anion;[6] owing to insufficient resolution in conjunction with additional small acetyl proton hyperfine splitting, we have not yet been able to make further assignments.

Nevertheless, these results are remarkable because there have been few stable radical cations reported which contain a carboxamide function[7] and none with an $NP(S)R_2$ group. This study shows that the 1,4-dihydropyrazine system is sufficiently π electron rich to accommodate the π accepting N-substituents C(O)Me and $P(S)Me_2$ without losing its propensity to be oxidized to a persistent 7π electron oxidation state.

Received, 1st July 1985; Com. 928

References

1 H. D. Hausen, O. Mundt, and W. Kaim, *J. Organomet. Chem.*, 1985, in the press.
2 W. Kaim, *Angew. Chem.*, 1981, **93**, 620, 621; *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 599, 600; *J. Am. Chem. Soc.*, 1983, **105**, 707.
3 R. Gottlieb and W. Pfleiderer, *Liebigs Ann. Chem.*, 1981, 1451.
4 W. Kaim, *Angew. Chem.*, 1984, **96**, 609; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 613; *Heterocycles*, 1985, **23**, 1363; *Acc. Chem. Res.*, 1985, **18**, 160.
5 W. Kaim, *Z. Naturforsch., Teil B*, 1981, **36**, 150; W. Kaim, U. Lechner-Knoblauch, P. Hänel, and H. Bock, *Chem. Ber.*, 1982, **115**, 1265; *J. Org. Chem.*, 1983, **48**, 4206.
6 P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 1962, **37**, 2811.
7 S. F. Nelson, S. C. Blackstock, and D. T. Rumack, *J. Am. Chem. Soc.*, 1983, **105**, 3115.