## Photocatalytic Systems.
XLVI.* The Photoinduced Decomposition of Tributylstannyl Chromate(VI) as Studied by ESR Spin Trapping

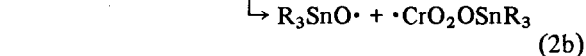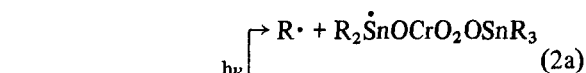D. REHOREK, W. WINKLER, R. WAGENER and H. HENNIG**

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In contrast to trialkyl and triaryltin halides which photodecompose according to eqn. (1) only during irradiation with UV light [1], the recently described chromates [2] show a strong photosensitivity in the visible region.

$$R_3SnX \xrightarrow{h\nu} R\cdot + R_2\dot{S}nX \qquad (1)$$
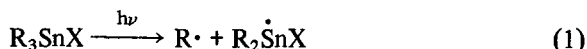
In order to answer the question whether the photoreaction of trialkyltin chromates is analogous to that of the halides, *i.e.* scission of the Sn-alkyl bond (2a), or it is a Cr–O bond scission (2b), we have performed ESR spin trapping experiments with tri(n-butyl) stannyl chromate(VI), the preliminary results of which are reported here.

$$R_3SnOCrO_2OSnR_3 \xrightarrow{h\nu} \begin{cases} R\cdot + R_2\dot{S}nOCrO_2OSnR_3 & (2a) \\[2ex] R_3SnO\cdot + \cdot CrO_2OSnR_3 & (2b) \end{cases}$$

Experimental

All experiments were performed at room temperature both under aerobic and anaerobic conditions using nitrosodurene (*ND*), phenyl N-tert-butyl nitrone (*PBN*) and 2-methyl-2-nitrosopropane (*MNP*) as spin traps, respectively. Anaerobic solutions were prepared by bubbling nitrogen for 15–20 minutes immediately before used. The samples containing the spin trap and tributyltin chromate were sealed an irradiated directly within the ESR cavity by a 200 W high pressure mercury lamp (HBO 200, VEB

Narva Berlin). Glass filters were used to cut off the light $\lambda < 400$ nm. In the experiments with *MNP* additional glass filters were used to prevent decomposition of the spin trap by red light.

Benzene and CH_2Cl_2, purified by standard methods, were used as solvents. In a series of experiments carbon halides, such as CCl_4, tert-butyl chloride, tert-butyl bromide and isopropyl iodide were added to the solutions.

Spin traps were obtained from VEB Laborchemie Apolda. Tributyltin chromate was prepared according to the method described previously [2].

Results and Discussion

Immediately after starting irradiation ($<1s$) strong signals with g values in the range of 1.95 to 1.98 could be detected. No interference by spin traps was observed. Based on the ^{53}Cr hyperfine splitting and g values, these signals were assigned to chromium-(V) species, albeit the structure could not be established in all cases. Details on Cr(V) formation will be reported elsewhere [3].

In the presence of spin traps additional signals were found, due to adducts of short-lived radicals to nitroso compounds and nitrones respectively. Hyperfine splitting constants together with assignments based on literature data [1, 4–6] are given in Table I. With nitrosodurene, spin adducts of butyl radicals could be readily observed in benzene solution. Under both anaerobic and aerobic conditions an additional triplet with $a_N = 2.38$ mT was detected, and tentatively assigned to the tributylstannoxyl ($Bu_3SnO\cdot$) spin adduct. It should be noted that a similar signal is also observed in the case of triphenylstannyl chromate [3]. In this case the formation of phenyloxy spin adduct to *ND* is unlikely [4]. Therefore, we assume the triplet with $a_N = 2.38$ mT to be the stannoxyl spin adduct rather than the butoxyl adduct. Further support for this assignment was obtained from the studies with *PNB* and *MNP* as spin traps.

With *MNP*, two spin adducts have been detected under anaerobic conditions. There is no doubt that one of them can be assigned to the butyl radical [5]. The other signal is identical with the nitroxide observed by Davies and Hawari [6] during the reaction of tributylstannyl radicals with 2-nitro-2-methylpropane. It is therefore assigned to the tributylstannoxyl spin adduct to *MNP*. The tin hyperfine splitting which is reported by Davies and Hawari [6] to be only 0.45 mT cannot be resolved in our case, probably due to line broadening by paramagnetic chromium species. In the presence of oxygen, the spin adducts of butoxyl radicals ($BuO\cdot$) to *MNP* are

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TABLE I. Hyperfine Splitting Constants of Spin Adducts (in mT).

Radical	Spin Trap	Solvent	a_N	a_H
n-Bu•	*ND*	CH_2Cl_2	1.37 ± 0.02	1.09 ± 0.02[a]
n-Bu•	*ND*	C_6H_6	1.34 ± 0.02	1.04 ± 0.02[a]
Bu_3SnO•	*ND*	C_6H_6	2.38 ± 0.03[b]	
n-Bu•	*MNP*	CH_2Cl_2	1.52 ± 0.02	0.99 ± 0.02[c]
n-Bu•	*MNP*	C_6H_6	1.51 ± 0.02	1.00 ± 0.02[c]
Bu_3SnO•	*MNP*	CH_2Cl_2	2.81 ± 0.04[d]	
Bu_3SnO•	*MNP*	C_6H_6	2.88 ± 0.04[e]	
BuO•	*MNP*	C_6H_6	2.84 ± 0.04	0.13 ± 0.02 (2H)
n-Bu•	*PBN*	CH_2Cl_2	1.46 ± 0.02	0.33 ± 0.02
n-Bu•	*PBN*	C_6H_6	1.46 ± 0.02	0.34 ± 0.02
BuO•	*PBN*	CH_2Cl_2	1.36 ± 0.02	0.22 ± 0.02
BuO•	*PBN*	C_6H_6	1.36 ± 0.02	0.20 ± 0.02
Bu_3SnO•	*PBN*	C_6H_6	1.41 ± 0.02	0.21 ± 0.02[f]

[a] $a_{13C} = 0.70 \pm 0.02$. [b] $g = 2.0059 \pm 0.0005$. [c] $a_{13C} = 0.44 \pm 0.02$. [d] $g = 2.0056 \pm 0.0005$. [e] $g = 2.0053 \pm 0.0005$. [f] Sn-hfs not resolved.
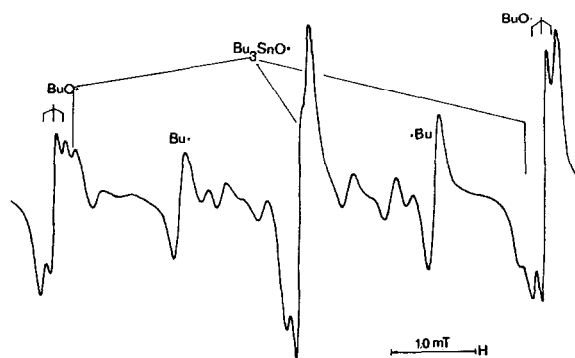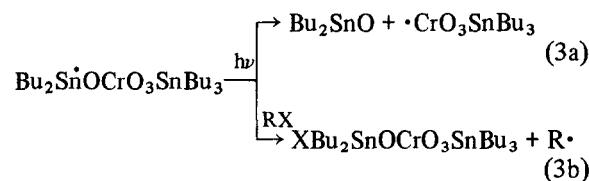

Fig. 1. ESR spectrum of spin adducts obtained during the photolysis of $(Bu_3Sn)_2CrO_4$ in the presence of 2-methyl-2-nitrosopropane (room temperature, CH_2Cl_2).

also detected (see Fig. 1). Oxygen reacts very rapidly with alkyl radicals forming alkylperoxyl radicals (ROO•) [7] which are trapped by *MNP*. However, these spin adducts are very unstable and decompose under formation of alkoxyl radicals [8] which may be trapped again to give the observed alkoxyl spin adduct.

Similarly, the radical Bu_3Sn• also reacts with oxygen very rapidly [9]. However, only traces of alkyl spin adducts other than the n-butyl adduct are observed in the presence of alkyl halides, *e.g.* CH_2-Cl_2, CCl_4, i-PrBr, i-PrI, t-BuCl, t-BuBr, which are known to be very efficient scavengers for stannyl radicals [10]. Therefore, we can conclude that tri-butylstannyl radicals (Bu_3Sn•) are only by-products of minor extent, if at all. The observed alkyl radicals which are formed by halogen abstraction from alkyl

halides have to be produced by species other than Bu_3Sn• radicals. There are some evidences for Cr(V) being responsible for this reaction [11], however, an active role of stannyl radicals formed according to eqn. (2a) cannot be ruled out completely. Since these species are expected to cleave very rapidly into Cr(V) and diamagnetic tin intermediates, *e.g.* Bu_2SnO, low yields of halogen abstraction are explainable, see eqn. (3).

$$Bu_2\overset{\bullet}{Sn}OCrO_3SnBu_3 \xrightarrow[\text{RX}]{h\nu} \begin{array}{l} \rightarrow Bu_2SnO + •CrO_3SnBu_3 \quad (3a) \\ \\ \rightarrow XBu_2SnOCrO_3SnBu_3 + R• \quad (3b) \end{array}$$

On the other hand, the occurrence of Bu_3SnO• radicals, *i.e.* the validity of eqn. (2b), is proved by spin trapping with *PBN*. At low concentration of *PBN* (*ca.* 10^{-3} *M*) only signals of butyl spin adducts could be detected under anaerobic conditions, whereas in the presence of oxygen butoxyl radicals are trapped too. The increase of *PBN* concentration up to about 1 *M* led to a significant decrease of the concentration of butyl spin adduct. Unlike results obtained under anaerobic conditions, there appeared a new spin adduct which is assigned to the Bu_3SnO• radical. Hyperfine splitting constants a_N and a_H were very similar to the parameters of the butoxyl adduct. However, the thermal and photochemical behaviour is quite different. Whereas butyoxyl spin adducts to *PBN* are persistent for at least several ten minutes under our conditions, the tributylstannoxyl spin ad-

duct is thermally and photochemically unstable. From the spin trapping experiments using various *PBN* concentrations it may be concluded that butyl radicals are formed by decomposition of tributylstannoxyl radicals (4), rather than by a primary photochemical reaction, eqn. (2a).

$$Bu_3SnO\cdot \rightarrow Bu\cdot + Bu_2SnO \qquad (4)$$
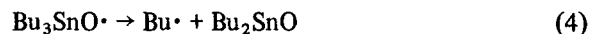
Bu_2SnO does polymerize to give polymeric stannoxane [12] as we have established by product analysis [3].

References

1 E. G. Janzen and B. J. Blackburn, *J. Am. Chem. Soc.*, *91*, 4481 (1969).

2 R. Wagener, M. Ackermann and H. Hennig, *Z. anorg. allg. Chem.*, in press.

3 D. Rehorek, W. Winkler, R. Wagener and H. Hennig, *J. Organomet. Chem.*, submitted for publication.

4 S. Terabe, K. Kuruma and R. Konaka, *J. Chem. Soc. Perkin II*, 1252 (1973).

5 C. Lagercrantz, *J. phys. Chem.*, *75*, 3466 (1971).

6 A. G. Davies and J. A. A. Hawari, *J. Organomet. Chem.*, *201*, 221 (1980).

7 J. K. Thomas, *J. Phys. Chem.*, *71*, 1919 (1967).

8 J. A. Howard and J. C. Tait, *Can. J. Chem.*, *56*, 176 (1978).

9 J. A. Howard, J. C. Tait and S. B. Tong, *Can. J. Chem.*, *57*, 2761 (1979).

10 D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, *90*, 7047 (1968).

11 D. Rehorek, W. Winkler, R. Wagener and H. Hennig, *Z. Chem.*, in press.

12 W. Trotter and A. C. Testa, *J. Am. Chem. Soc.*, *90*, 7044 (1968).