

ESR STUDY OF METAL REDUCTION OF α -KETOPHOSPHONATES.
FORMATION OF SEMIDIONES⁽¹⁾ FROM THE CORRESPONDING KETYLs.

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Owing to the presence of a phosphoryl moiety, α to a carbanionic like carbon, the knowledge of the electronic structure of α -phosphonyl ketyl⁽²⁾ ($\text{RC}(\ddot{\text{O}})\text{P}(\text{O})(\text{OR}')_2\text{M}^+$) may provide information with regard to structural problems of current interest⁽³⁾. The present ESR study was undertaken to investigate the electronic structure and chemical behaviour of these phosphonyl ketyl⁽²⁾. In addition we wish to compare these species, with the corresponding isoelectronic nitroxydes, previously studied in our laboratory⁽⁴⁾. A part of our first results is presented here.

In contrast to the mirror-metal technique, we developed an ESR cell⁽⁵⁾, which allows a permanent contact between the sample solution and the metal during the whole ESR observation time.

The solutions of α -ketophosphonate, in a mixture of highly purified tetrahydrofuran and dimethoxyethane (2/1) were reduced under an S-argon atmosphere. Two alkali metals -potassium and lithium- were used and the results obtained for seven different α -ketophosphonates are listed in table I.

The phosphorus splitting the g value and transient characteristics of $^6\text{Li}^+$ and $^7\text{Li}^+$ (Table I) are in good agreement with a phosphonyl ketyl structure⁽⁷⁾. This conclusion is also borne out by the following facts : (a) A phosphorus splitting of 27.2 G has been reported⁽⁸⁾ for the radical $(\text{HOCH}_2)_2\text{P}(\text{O})\dot{\text{C}}\text{HOH}$ and (b) the small increase of the g value with regard to the mean g value of a dialkylketyl (2,0034-2,0037)⁽⁹⁾ corresponds to the stabilisation of the carbanionic form of the ketyl by the adjacent phosphorus group. The same trend of the g value has been reported⁽¹⁰⁾ for the ketyl⁽²⁾s of acetyltrimethylsilane and isobutyryltrimethylsilane.

The lack of ESR signals during the lithium-reduction of $^3,^4$ and 5 , can be accounted for by the fast disproportionation⁽¹¹⁾ of the resulting lithium ketyl⁽²⁾s which bear hydrogen atoms in an α position.

At least two mechanisms can be postulated to explain the formation of semidiones in the metal reduction of α -ketophosphonates (viz scheme I).

Table I : Radical-anions observed during the metal-reduction
of α -ketophosphonates $RC(O)P(O)(OR')_2$

R	R'	K	θ	Li	θ	
tBu	Et	λ	Semidione ^(i,j)	-80°C	λ^-Li^+ (k)	
	iPr	λ'		to room temp.	$a_p = 23.7$ G $g = 2.0039$	<-50°C
Ad ^(l)	Et	λ	Semidione ^(m)	"	λ^-Li^+ (k) $a_p = 24.2$ G $g = 2.0039$	<-50°C
iPr	Et	λ	Semidione	"	NO signals	-80°C to room temp.
	iPr	λ'				
Et	Et	λ	Semidione	-70°C	"	"
Me	Et	λ	Semidione	-80°C	"	"

i - Semidione : $RC(\bar{O})=C(\dot{O})R$. For all the semidiones reported here the a_H and g values are similar to those reported in the literature⁽⁶⁾.

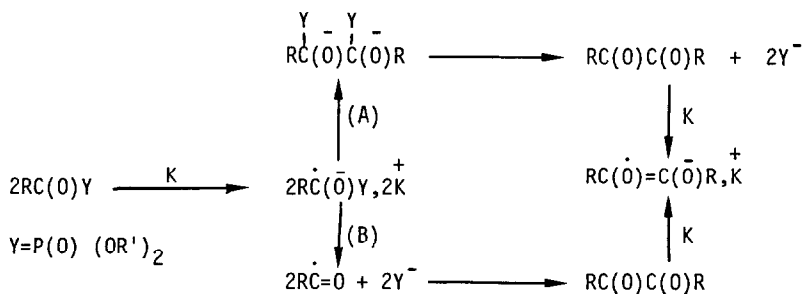
j - In addition to the signals of the di *t*-butyl semidione a two-line spectrum resulting from the *t*-butylglyoxal radical anion $tBu\dot{G}^-K^+$ ($a_H = 8.2$ G, $g = 2.0048$) is observed below -20°C.

k - In addition to the signals of the ketyls small amounts of the corresponding semidiones are detected.

l - Ad = adamantyl

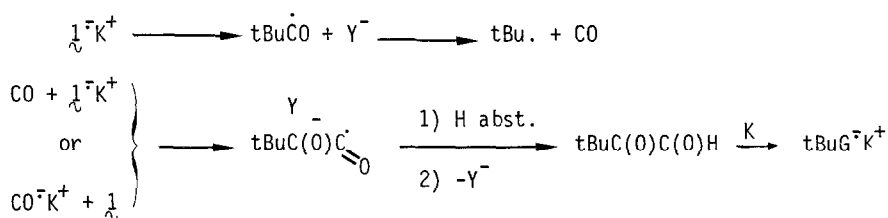
m - $a_H = 0.20$ G (6H)

SCHEME I :



Dimerisation (pathway A) is very common for ketyls in non protic solvents and according to the good leaving ability of the phosphonate group the resulting dialcoholate might be expected to form the diketone. The same sequence is believed to account for the formation of α -hydroxy ketone and the ESR detection ⁽¹²⁾ of semidione during the acyloin condensation. Pathway B has been stressed ⁽¹³⁾ as a possible explanation of the formation of benzoin after electrolysis of dialkyl aroyl phosphonates in acetonitrile. Its occurrence during the potassium reduction of $\dot{\text{C}}_6$ (Table I, j) is substantiated by the detection and the identification ⁽¹⁴⁾ of the tertibutylglyoxal radical anion which formation is accounted for by the very fast decarbonylation of the pivaloyl radical (k_D 600s^{-1} at -50°C) ⁽¹⁵⁾. The carbon monoxide which is evolved (or perhaps its radical anion) could then be incorporated ⁽¹⁶⁾ by $\dot{\text{C}}_6^-$ or $\dot{\text{C}}_6$ (viz scheme II).

SCHEME II



We believe that pathway A is the predominant pathway, the experimental observations which prompted this conclusion are the following : Firstly as the temperature is raised the signals of $\text{tBuG}^- \text{K}^+$ disappear while the signals of the ditertibutyl semidione are intensified. Secondly in the presence of dibenzo-18-crown-6 the signals of $\text{tBuG}^- \text{K}^+$ are greatly enhanced and become predominant. But it is known ⁽¹⁷⁾ that crown ether complexation with the counterion reduces the effectiveness of the dimerisation of radical anions and accordingly favors here the decomposition.

Our results show that the lithium α phosphonyl ketyls which cannot disproportionate are persistent enough in non-protic solvent at -50°C to be detected and studied by ESR. On the other hand, potassium homologs are readily converted into the corresponding semidiones mainly via dimerisation. This difference of behaviour could be a consequence of different modes of association.

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References and notes

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