Ready Homolytic Splitting of an Organocobalt(III) Complex under the Action of Protons: New Sources of Free Radicals

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Received October 26, 1982

The action of acids upon alkyl derivatives of electropositive elements generally results either in protolysis or in β-elimination resulting in the formation of related alkanes or alkenes. Nevertheless, in some complexes transition metal–carbon σ-bonds may yield to homolytic splitting more readily if other ligands are protonated. In the particular case of octahedral organocobalt(III) complexes, such protonations would shake loose initial eighteen-electron structures, which may result in weakening of the metal–carbon bond and eventually lead to its homolysis. this assumption seems to be supported by recent studies [1–4] of the decomposition of organocobalt chelates in acidic media. However, none of these papers dealing with the best known type of the complexes, *viz.* that with an equatorial tetradentate ligand, provided straightforward evidence for the intermediacy of free radicals. Moreover, the most advanced study [4] showed that the protonation of a tetradentate ligand accelerated β-elimination to the same extent as coupling of radicals.

We have found that alkylcobalt(III) complexes belonging to a newly reported [5] type readily undergo homolytic splitting under the action of protons, with direct evidence for the effective generation of alkyl free radicals being obtained. Also, this feature of the complexes has been used for modelling coenzyme B_{12}-dependent dehydratation of α-glycols. These studies are outlined below.

In acidic media ions of alkyl-*mer*-[N-(2-aminoethyl)-7-methylsalicylideneiminato](ethylenediamine) cobalt(+1) ([RCo(7-Mesalen)(en)]$^+$) decay quite readily. Thus, the complexes with R = Me, higher primary alkyl and sec-alkyl decompose in 1*M* aqueous perchloric acid at 20–25 °C within several hours, minutes and seconds respectively. All the products of the disproportionation and coupling of the alkyl radicals are formed in this reaction (Table I).

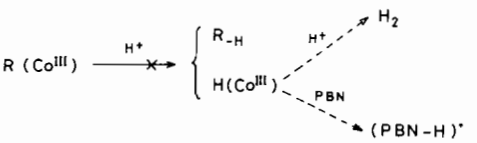
Although the yields of RH alkanes are considerably higher than those of alkenes, the protolysis of the Co–C bonds does not contribute substantially to the overall process, which was proved by means of isotope-label technique. *Viz.*, ethane formed from the ethylcobalt complex in 1 *M* solution of $DClO_4$ in D_2O included less than 5% of C_2H_5D molecules. This result evidently reveals that the excesses of the RH alkanes over the alkenes are essentially due to the abstraction of hydrogen atoms from chelating ligands by alkyl free radicals, rather than due to the protolysis.

TABLE I. Hydrocarbon Products from the Decomposition of [RCo(7-Mesalen)(en)]$^+$ Complexes in Acidic Solution.[a]

R	Relative Yield[b]		
	R_{-H}	RH	R_2
Me		1	23
Et	1	3.2	2.4
Bu^n	1	3.8	[c]
Pr^i	1	1.4	0.41

[a] 1 *M* aqueous solution of $HClO_4$ as medium; initial concentrations of the complexes, 20 m*M*; 20 °C. [b] Determined by GC head-space analysis after the complete decomposition of the complexes. [c] Not assayed.

Further study indicated that the decompositions are not affected appreciably by β-elimination. Otherwise one would expect that certain products derived from an intermediate hydride complex could be found. On the contrary, we failed to detect molecular hydrogen after conventional runs as well as the spin adduct of hydrogen atom in the course of those carried out in the presence of phenyl-N-tert-butylnitrone (PBN):



The formation of alkyl free radicals in the course of the reactions under investigation was directly proved by spin-trapping technique. Thus the complexes decomposing in phosphate buffer solutions in the presence of tert-nitrosobutane (TNB) or PBN gave the ESR signals characteristic of the spin adducts of the proper alkyl radicals (Table II). Furthermore, kinetic measurements using PBN demonstrated the growth rate of the ESR signals to be pH-dependent. The pattern of these relationships is exemplified by Fig. 1. As the following consideration is to reveal, they definitely indicate that protons are involved in the process yielding alkyl free radicals. Under conditions used, *viz.* at low conversions and at a large excess of the trap, one can treat the formation of the

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TABLE II. ESR Hyperfine Splitting Constants of Nitroxide Radicals, RN(Ó)Bu^t, Detected in the Course of the Decomposition of [RCo(7-Mesalen)(en)]$^+$ Complexes in the Presence of tert-Nitrosobutane.[a]

R	Splitting Constants, G		
	^aN	$^aH(\beta)$	$^aH(\gamma)$
Me	16.8	14.7	
Et	16.8	11.3	0.6
Bu^n	16.8	11.3	0.7
c-C_6H_{11} [b]	14.8	1.7	

[a]Phosphate buffer MeOH–H_2O 1:2 (v/v) solutions as media, 20 °C. [b]In this case a more intricate ESR spectrum was observed. It can be interpreted as the superimposition of two signals with rather close g-factors. One of the signals is apparently due to the cyclohexyl adduct. Analysis of the spectrum also suggests that the other, more multiple signal is related to a spin adduct of a radical resulting from abstraction of a hydrogen atom from the tridentate ligand.

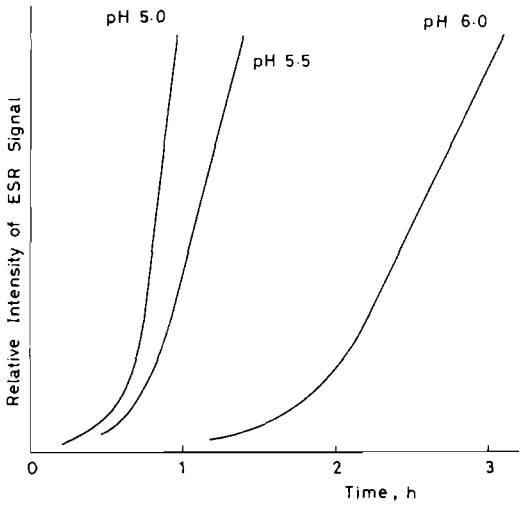

Fig. 1. Decomposition of the [EtCo(7-Mesalen)(en)]$^+$ complex in the presence of PBN: intensities of the ESR signal as functions of time at various pH. (Phosphate buffer MeOH–H_2O 1:2 (v/v) solutions as media, 20 °C; initial concentration of the complex, 5 m*M*; that of PBN, 0.1 *M*).

spin adducts as a pseudo-first order process and neglect succeeding reactions involving these stable free radicals. Consequently, the slopes of the kinetic curves presented at Fig. 1 are approximately proportional to R$^\cdot$. Hence the linear parts of the curves correspond with the concentration having reached stationary values, $[R^\cdot]_{st}$. Thus comparison of these curves enables one to conclude that $[R^\cdot]_{st}$ increases as pH is lowered. Obviously, such an antibatic dependence on pH must hold qualitatively true for the stationary rate of the formation of alkyl free radicals. In addition, the shape of the curves is indicative of an induction period, which is probably due to a consecutive mechanism of this reaction*. Then a clear-cut symbatic correlation between pH and the duration of the induction period wholly agrees with the involvement of protons in the process.

TABLE III. Dehydratation of α-Glycols Conjugated with the Decomposition of the [EtCo(7-Mesalen)(en)]$^+$ complex.[a]

Substrate	Products[b]	Yield, %[c]
CH_2OHCH_2OH	MeCHO	5.0
$MeCHOHCH_2OH$	Me_2CO	26
	EtCHO	0.24

[a]0.5 *M* solutions of $HClO_4$ in the 1:1 (v/v) mixtures of glycols with water as media; initial concentration of the complex, 19 m*M*; 20–25 °C. [b]Identified by GC and, in the form of 2,4-dinitrophenylhydrazones, by TLC. [c]Determined by GC analysis after the complete decomposition of the complex and referred to the initial amount of the latter.

Thus, the organocobalt(III) complexes in question can generate alkyl free radicals under mild conditions and at a conveniently regulated (pH-controlled) rate. We have tried and used this feature of the complexes for modelling the coenzyme B_{12}-dependent dehydratation of α-glycols, which is generally considered [6] to proceed *via* a free-radical mechanism. Some early results are summarized in Table III. To our knowledge, this is the first case where an organocobalt model of coenzyme B_{12} has been proved to induce dehydratation of glycols at room temperature and in the dark. The model reaction is still lacking both catalytic character of the enzymatic one and its 'counter-thermodynamic' specificity. Namely, the latter results in formation of aldehydes while ketones emerge as predominant products of the former. Nevertheless, despite these differences, results of the present study give certain ground to the speculation that protonation-deprotonation or some related polar interactions may control the dissociation of the Co–C bond of coenzyme B_{12} in ferment systems, thus triggering the biological dehydratation of glycols as well as other coenzyme B_{12}-dependent reactions.

Acknowledgement

We thank Professor R. Kh. Freidlina and Dr. A. D. Ryabov for helpful discussions, and Drs. Yu. S. Nekrasov and D. V. Zagorevsky for mass-spectral isotopic analyses.

*It is appropriate to point out that preliminary results of a spectrophotometric study, which is under way, also indicate a complex kinetics with at least two coloured intermediates.

References

1 C. W. Fong and M. D. Johnson, unpublished work cited in the review: D. Dodd and M. D. Johnson, *J. Organometal. Chem., 52,* 1 (1973); p. 66, Ref. 235.
2 B. T. Golding, T. J. Kemp, P. J. Sellers and E. Nocci, *J. Chem. Soc., Dalton Trans.,* 1266 (1977).
3 N. W. Alcock, M. P. Atkins, B. T. Golding and P. J. Sellers, *J. Chem. Soc., Dalton Trans.,* 337 (1982).
4 H. J. Gjerde and J. H. Espenson, *Organometallics, 1,* 435 (1982).
5 I. Levitin, A. Sigan, E. Kazarina, G. Alexandrov, Yu. Struchkov and M. Vol'pin, *J. Chem. Soc., Chem. Commun.,* 441 (1981).
6 H. Dugas and C. Penney, 'Bioinorganic Chemistry. A Chemical Approach to Enzyme Action', Springer, New York, Heidelberg, Berlin (1981), Sect. 6.6.