dass eine SeO_3-Lösung in SO_2Cl_2 sich mit Thionylchlorid nach der Gleichung

$$SeO_3 + SOCl_2 = SeO_2 + SO_2Cl_2$$

in exothermer Reaktion unter Bildung von Selendioxid umsetzt. Diese Reaktion lässt sich bei $-10\,°C$ auch in SO_2 als Lösungsmittel durchführen, wobei das entstandene SO_2Cl_2 spektroskopisch und nach Hydrolyse als $BaSO_4$ nachgewiesen werden kann. Mit Phosphortrichlorid reagiert SeO_3, wenn man SO_2 als Lösungsmittel verwendet, analog nach der Gleichung

$$SeO_3 + PCl_3 = SeO_2 + POCl_3.$$

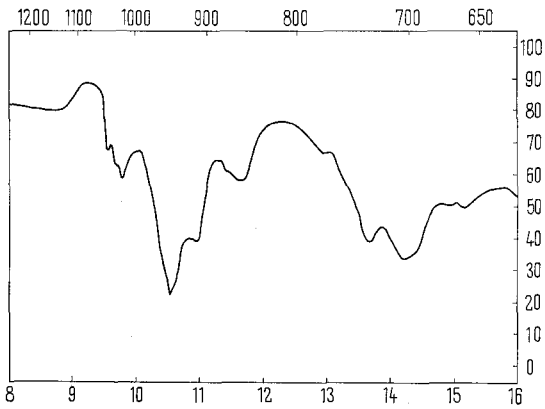
Lässt man hingegen eine Lösung von SeO_3 in SO_2Cl_2 als Lösungsmittel auf PCl_3 einwirken, so entsteht nicht das erwartete SeO_2; dieses setzt sich vielmehr in bekannter Weise[5] weiter um nach den Gleichungen

$$SeO_2 + 2\,PCl_3 = 2\,POCl_3 + Se$$

$$2\,Se + SO_2Cl_2 = Se_2Cl_2 + SO_2$$

$$Se_2Cl_2 + 3\,SO_2Cl_2 = 2\,SeCl_4 + 3\,SO_2,$$

so dass als Endprodukt $SeCl_4$ erhalten wird.



SeO_3 gelöst		$(SeO_3)_4$ krist.	
cm^{-1}	μ	cm^{-1}	μ
1055	9,5 s	1055	9,5 st
1035	9,65 s (sch)	1044	9,6 st
1025	9,75 m		
952	10,5 st	956	10,55 st
913	10,95 m		
862	11,6 m	827	12,1 s
735	13,6 m	735	13,6 st (sch)
704	14,2 st		
674	14,85 ss	674	14,85 sst

s = schwach; m = mittelstark; st = stark; sch = Schulter; sst = sehr stark; ss = sehr schwach.

Summary. Selenium trioxide may be dissolved in sulphuryl chloride and in phosphoryl chloride at room temperature without decomposition. Reactions of selenium trioxide with thionyl chloride and phosphorus trichloride are carried out in sulphuryl chloride as a solvent. For the first time, an IR-spectrum of dissolved selenium trioxide is recorded.

E. CLASS[6]

Institut für anorganische Chemie, Universität Basel (Schweiz), 21. Dezember 1965.

[5] A. MICHAELIS, Z. Chemie (2), *6*, 467 (1870). – H. DANNEEL und F. SCHLOTTMANN, Z. anorg. allg. Chem. *212*, 225 (1933).

[6] Zu Dank verpflichtet sind wir Herrn. Prof. Dr. H. ERLENMEYER für wertvolle Anregungen und Ratschläge, Herrn Dr. B. PRIJS für die Hilfe bei der Abfassung des Manuskriptes.

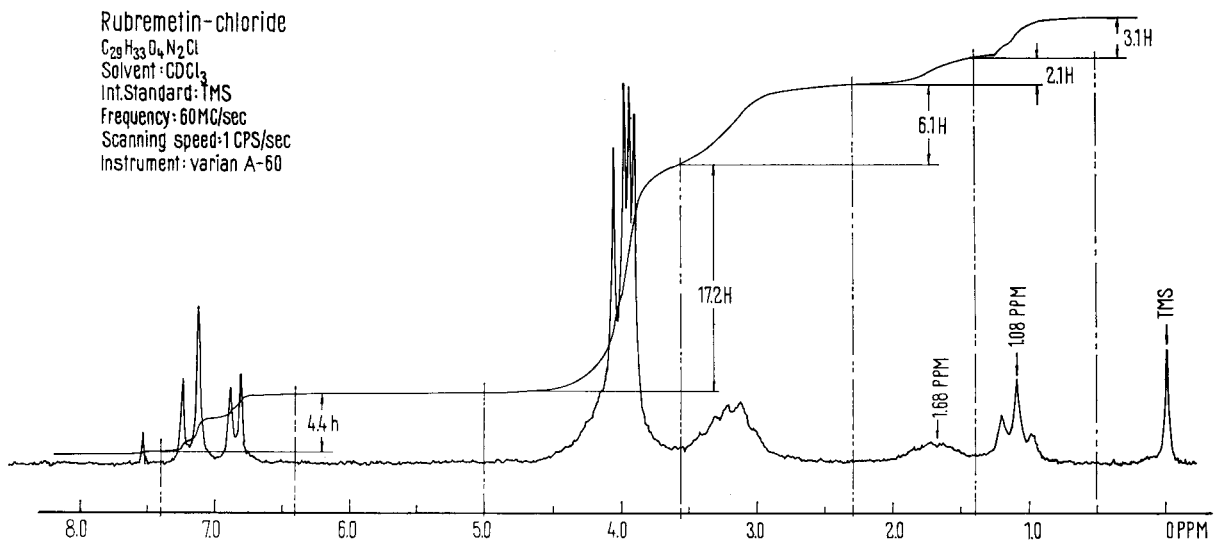
The Rubremetinium and Rubremetaminium Cations

Emetine (I) can be converted by means of mild oxidizing agents such as ferric chloride, iodine, bromine or mercuric acetate into optically active, orange-red salts of a quaternary, monoacidic base[1]. The cation of these salts is called the rubremetinium cation. Similarly emetamine (II), a minor Ipecacuanha alkaloid[2], can be dehydrogenated by bromine and by mercuric acetate to give a corresponding but different product based upon the rubremetaminium cation[3,4].

Of the various structures suggested for the rubremetinium cation, only two have deserved serious consideration[1]; these are (IV)[5] $C_{29}H_{33}O_4N_2^+$ and (III)[6] $C_{29}H_{31}O_4N_2^+$. There is strong chemical evidence[1] in support of the former structure and the results obtained from the preparation of model compounds[7,8] are in agreement. Confirmation of structure (IV) by physical methods is outlined below.

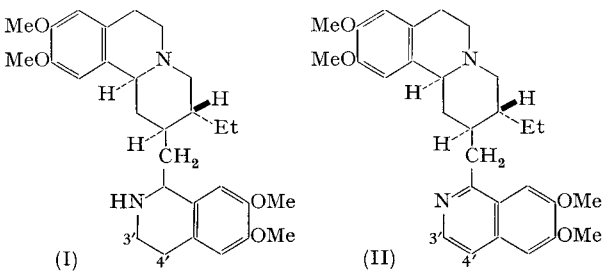
The NMR spectrum of rubremetinium chloride (see Figure) shows a broad multiplet at 8.32 τ corresponding to the methylene protons of the ethyl side chain. When the position and multiplicity of this signal are compared with the signals given by the ethyl side chain of the salt (V) measured under the same conditions[9] (triplet 3H at 8.64 τ and quartet 2H at 7.18 τ) it is clear that in the rubremetinium cation, the ethyl residue is attached to a CH group and not to a pyridinium nucleus in keeping with structure (IV).

The NMR spectrum of rubremetaminium chloride run in $CDCl_3$ also shows a broad multiplet centred at 8.3 τ (cf. rubremetinium chloride above). This is in agreement with structure (IV, double bond at 3′, 4′) rather than with structure (III, double bond at 3′, 4′). Further, when carefully controlled conditions are used, rubremetinium



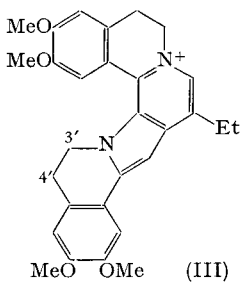
chloride and rubremetaminium chloride afford good mass spectra[10] by direct inlet; the parent ions appear at m/e 473 ± 1 and m/e 471 ± 1, respectively. The nitrogen rule[11] allows the true values 473 and 471 to be assigned to the parent cations (corresponding to 472 and 470, respectively, for the products of thermal Hofmann degradation[12]). These results give strong support to structures (IV) and (IV, double bond at 3′, 4′) for these two salts.

The foregoing studies have been extended by work on simple model compounds and details of the syntheses involved will be published separately by the various groups.

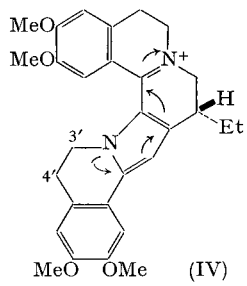


(I)

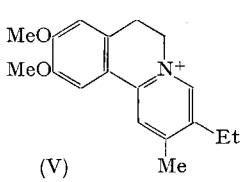
(II)



(III)



(IV)



(V)

Zusammenfassung. Spektroskopische und massenspektrometrische Daten bestätigen die Struktur (IV) für das Rubremetiniumkation. Rubremetaminiumsalze besitzen analoge Struktur mit einer zusätzlichen Doppelbindung in 3′, 4′-Stellung.

A. Brossi[13], M. Gerecke,
A. R. Battersby, R. S. Kapil,
Y. Ban and M. Terashima

Forschungsabteilung der F. Hoffmann-La Roche and Co. AG, Basel (Switzerland), The Robert Robinson Laboratories, University of Liverpool (England), and School of Medicine, Hokkaido University, Sapporo (Hokkaido, Japan), December 6, 1965.

[1] For review see H. T. Openshaw, Chem. Soc. spec. Publication *3*, 28 (1955).

[2] F. L. Pyman, J. chem. Soc. *111*, 419 (1917); W. H. Brindley and F. L. Pyman, J. chem. Soc., 1067 (1927); A. R. Battersby, G. C. Davidson, and B. J. T. Harper, J. chem Soc., 1744 (1959).

[3] P. Karrer, C. H. Eugster, and O. Rüttner, Helv. chim. Acta *31*, 1219 (1948).

[4] A. R. Battersby, Chem. Soc. spec. Publication *3*, 36 (1955).

[5] A. R. Battersby, H. T. Openshaw, and H. C. S. Wood, Experientia *5*, 114 (1949); H. T. Openshaw and H. C. S. Wood, J. chem. Soc., 391 (1952).

[6] R. F. Tietz and W. E. McEwen, J. Am. chem. Soc. *75*, 4945 (1953).

[7] A. R. Battersby and T. P. Edwards, Chem. Soc. spec. Publication *3*, 28 (1955).

[8] Y. Ban and M. Terashima, Tetrahedron Lett. *22*, 796 (1961).

[9] M. Gerecke and A. Brossi, Helv. chim. Acta, *47*, 1117 (1964).

[10] A. R. Battersby and R. S. Kapil, forthcoming publication.

[11] J. H. Beynon, *Mass Spectrometry and its Applications to Organic Chemistry* (Elsevier, London 1960), p. 309.

[12] M. Hesse, W. Vetter, and H. Schmid, Helv. chim. Acta *48*, 674 (1965).

[13] Present address: Hoffmann-La Roche Inc., Nutley 10, N.J. (USA).