

Vapour-liquid equilibrium data have been determined for systems which are non-azeotropic, in which the second component is carbon tetrachloride,<sup>35</sup> chloroform,<sup>36</sup> formic acid,<sup>37</sup> methanol,<sup>37</sup> acetic acid,<sup>37</sup> ethanol,<sup>38,39</sup> acetone,<sup>36,37,39</sup> isopropanol,<sup>32</sup> benzene<sup>34</sup> and toluene.<sup>34</sup> The ternary system diethyl ether-ethanol-water is also non-azeotropic.<sup>38</sup>

## 12.4. Chemical Properties

The ether grouping is relatively unreactive, but there are nevertheless some reactions of interest.

**12.4.1. Oxidation.** On exposure to oxygen or air, diethyl ether forms non-volatile, explosive peroxides.<sup>40</sup> When peroxidised ether is evaporated, the peroxides concentrate in the residue, which becomes liable to undergo violent explosion. Accordingly, when ether is to be used as a solvent, it should be tested for peroxides before use<sup>41</sup> and, if present, the peroxides should be removed by adding a suitable reducing agent, e.g. shaking with aqueous acidic ferrous sulphate solution.

The autoxidation of ether is accelerated by light.<sup>42</sup> The progressive increase in the rate of peroxide formation has been attributed to the catalytic action of acetaldehyde, which is a known product of the decomposition of ether peroxide.

Whereas Clover considered the peroxide to be 1-ethoxyethyl hydroperoxide  $\text{CH}_3\text{CH}(\text{OOH})\text{OCH}_2\text{CH}_3$ , other workers<sup>43</sup> concluded that the primary products of ether oxidation were hydrogen peroxide and ethyl vinyl ether which hydrolyses to acetaldehyde and ethyl alcohol, and considered ether peroxide to be di-1-hydroxyethyl peroxide  $\text{CH}_3\text{CH}(\text{OH})\text{OOCH}(\text{OH})\text{CH}_3$  formed from the acetaldehyde and the hydrogen peroxide.

Another suggestion<sup>44</sup> is that the peroxide is 1-hydroxyethyl hydroperoxide.

The ether peroxides were however shown not to be the same as the peroxides made from acetaldehyde and hydrogen peroxide.<sup>46</sup> Rieche,<sup>46</sup> while considering that the first stage of peroxide formation was that suggested by Clover, showed that the expected 1-ethoxyethyl hydroperoxide was less explosive than the peroxides made by ether autoxidation, and later he considered the explosive peroxide to be a polymeric ethylidene peroxide formed by decomposition or hydrolysis of the initial hydroperoxide, as shown by the following scheme:

<sup>35</sup> Tyrer, *J. Chem. Soc.*, 1912, 101, 81.

<sup>36</sup> Ryland, *Am. Chem. J.*, 1899, 22, 390; *Chem. News*, 1908, 81, 15.

<sup>37</sup> Lecat, *Azeotropisme* (Lamartin, Brussels, 1918).

<sup>38</sup> Wuyts, *Bull. soc. chim. belg.*, 1924, 33, 178.

<sup>39</sup> Haywood, *J. Phys. Chem.*, 1899, 3, 317.

<sup>40</sup> Schönbein, *J. prakt. Chem.*, 1851, 52, 135; *J. Chem. Soc.*, 1852, 4, 132.

<sup>41</sup> A test is given in British Standard Specification BS:579/1957.

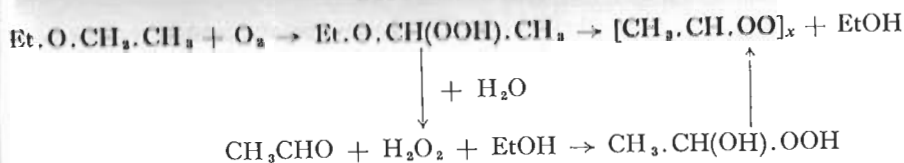
<sup>42</sup> Clover, *J. Am. Chem. Soc.*, 1922, 44, 1108.

<sup>43</sup> Wieland and Wiegler, *Ann.*, 1923, 431, 301.

<sup>44</sup> King, *J. Chem. Soc.*, 1929, 738.

<sup>45</sup> Milas, *J. Am. Chem. Soc.*, 1931, 53, 221.

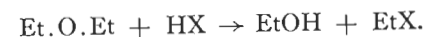
<sup>46</sup> Rieche and Meister, *Angew. Chem.*, 1936, 49, 101. Rieche, *ibid*, 1958, 70, 251.



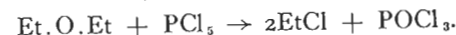
The autoxidation of ether in storage can be inhibited by the presence of hydroquinone,<sup>47,48,49,50</sup> pyrogallol,<sup>48</sup> propyl gallate,<sup>51</sup> pyrocatechol,<sup>49</sup> resorcinol,<sup>49</sup>  $\alpha$ -naphthol,<sup>50</sup>  $\beta$ -naphthol,<sup>50</sup> benzidine,<sup>48</sup> diphenylamine,<sup>47,50</sup> benzyl-p-aminophenol,<sup>52</sup> manganese or lead oxides,<sup>53,54</sup> sodium metal,<sup>53,54</sup> sodium amalgam,<sup>55</sup> or powdered iron.<sup>56</sup> The rates of autoxidation in the presence of various inhibitors have been shown to be decreased by storage in the dark.<sup>57</sup>

**12.4.2. Nitration.** Diethyl ether reacts violently with nitric acid giving oxidation and nitration products. At  $-15^\circ$  some ethyl nitrate is produced. The reaction can be effected more safely in the vapour phase; nitromethane, nitroethane and 2-nitroethyl ethyl ether are made at  $400^\circ$ .<sup>58</sup>

**12.4.3. Action of Acids.** Treatment with inorganic acids causes cleavage of the ether linkage. Cold concentrated hydriodic acid, concentrated sulphuric acid, or dilute inorganic acids at temperatures above the normal boiling point of the ether all lead to cleavage of one C-O bond, e.g.:



Cleavage of both the C-O bonds results from treatment with hot concentrated hydriodic acid or phosphorus pentachloride:



**12.4.4. Halogenation.** The nature of the products of halogenation depends upon the reaction conditions. High yields of a single product are not usually obtained. At ambient temperature and in the dark 1,2-dichlorethyl ethyl ether is obtained in 24 per cent yield. When the reactor was irradiated with light from a carbon arc at between  $-20^\circ$  and  $-30^\circ$ , the liquid phase chlorination of ether gave 1-chlorethyl

<sup>47</sup> Reimers, *Quart. J. Pharm. Pharmacol.*, 1946, 19, 172.

<sup>48</sup> Nolan, *Lancet*, 1933, 225, 129.

<sup>49</sup> Katsuno, *J. Soc. Chem. Ind., Japan*, 1944, 44, 903.

<sup>50</sup> Williams, *Chem. & Ind.* 1936, 580.

<sup>51</sup> Boehm and Williams, *Chem. Trade J.* 1944, 115, 70.

<sup>52</sup> Crawford and Turner (Carbide & Carbon Chemicals Corp.), USP 2,142,936 (1939).

<sup>53</sup> Demougin and Landon, *Bull. Soc. chim.*, 1935, 2, 27.

<sup>54</sup> Fisher and Baxter, *Mines Mag.* (Colorado School of Mines), August 1940, 30, 447.

<sup>55</sup> Bailey and Roy, *J. Soc. Chem. Ind.* 1946, 65, 421.

<sup>56</sup> Bicknese, *Pharm. Zentralhalle*, 1927, 68, 439.

<sup>57</sup> Hunter and Downing, *J. Soc. Chem. Ind.*, 1949, 68, 362.

<sup>58</sup> Hass and Hudgin, *J. Am. Chem. Soc.*, 1954, 76, 2692.