

THE HAZARD OF A PROPIONYL CHLORIDE—DIISOPROPYL ETHER MIXTURE

W.M.B. KÖNST

Development Section, Naarden-International, Postbox 2, 1400 CA Bussum (The Netherlands)

(Received April 8, 1980; accepted in revised form August 22, 1980)

Summary

An accident caused by an explosion of a stored mixture of propionyl chloride (PC) and diisopropyl ether (DIPE) led us to carry out thermodynamic calculations (CHETAH) and a literature study. The conclusion is drawn that mixtures of acid chlorides and ethers are very unstable and that storage will give rise to dangerous situations.

Introduction

When conducting chemical reactions, it is often necessary for various reasons to add progressively to the other reaction components one of the reagents dissolved in, or diluted with, an inert solvent to control the ensuing reaction. When this technique is used, it is essential that the solvent should not react with the reagent dissolved in it. In this paper we will describe an accident with a solution of propionyl chloride (PC) in diisopropyl ether (DIPE).

In the past such mixtures had been prepared several times on laboratory and pilot plant scale (100 l) and once on plant scale (3000 l) without causing any problems.

The accident

The relevant chemical process was the acylation of the anion of diethyl malonate in an ethanol—DIPE mixture with PC dissolved in DIPE (about 50% w/w). The procedures in the original literature (Lund, 1934; Breslow et al., 1944) used diethyl ether instead of DIPE. A mixture of PC and DIPE, meant for several batches, was prepared in advance in one production run (using a glass-lined mixing vessel) and was finally drawn off into the original drums. Half of the mixture was stored in non-coated DIPE drums, and the other half in the coated acid chloride drums.

The next day, during the starting-up of the malonate anion preparation,

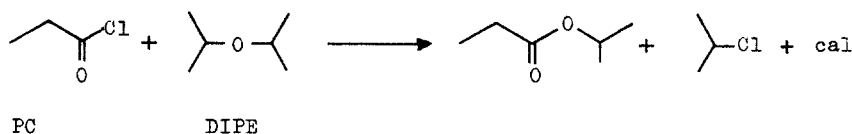
one of the PC-DIPE drums, stored in the vicinity of the reactor, exploded. At that moment, three operating personnel were present, but no one was injured. There was considerable damage but no fire. The lid (seamed joint) of the drum was rocketed upwards and a big vapour cloud was generated. The insulation of the reaction vessel, glass piping, electrical circuits and a flight of steel steps were badly damaged.

After the production unit was cleared, the screw caps of all drums were loosened and the drums transferred elsewhere. Then samples were taken and the contents of the drums quenched in water as soon as GLC analyses had been performed.

It was noticed that the contents of the exploded drum were still boiling.

Observations and general conclusions

GLC analysis of the contents of the exploded drum revealed that a reaction according to Scheme 1 had taken place almost quantitatively (see Table 1).



Scheme 1

Thus DIPE was cleaved by the acid chloride, giving isopropyl propionate and the volatile isopropyl chloride (B.P. 36°C). Because traces of propene were also found, the accident must be due to an explosion that occurred when the drum breakdown-pressure of 20–25 atm was surpassed upon formation of sufficient volatiles (thermal explosion).

Assuming a head space of 5% (10 l), that would mean an amount of about 200 l of gas, i.e. 8 moles. In a drum of 160 kg of 50% w/w PC-DIPE mixture, this amount of gas can be formed when only 1% of the acid chloride decomposes in some way to give hydrogen chloride, or from 1% of the DIPE giving propene.

Table 1 shows the results of GLC analysis of samples from a number of drums in comparison to the pure substances and a reference mixture.

If we analyze these data, the following conclusions may be drawn:

(1) The starting materials PC and DIPE, and also the mixture of these in the appropriate ratio, prove to be stable. No deterioration is observed in the injection port or on the column of the gas chromatograph.

(2) Compared to these reference materials, the other samples are not inert mixtures. All show the peaks of isopropyl chloride and isopropyl propionate in more or less abundance. This is why the contents of all drums were destroyed by quenching.

TABLE 1

GLC analysis ^a	Propene	Isopropyl chloride	PC	DIPE	Isopropyl propionate	Heavy metals ^d			Coating ^e
						Fe	Zn		
PC-DIPE mixture ^b	—	—	23	76	—	—	—	—	—
PC pure	—	—	100	—	—	—	—	—	—
DIPE pure	—	—	—	99	—	0.04	<0.1	—	—
Drum 1	—	1	20	73	3	13	<0.1	+	—
2	0.5	4	18	64	10	13	2.5	—	—
3	—	0.5	18	77	0.5	7	<0.1	+	—
4	—	0.5	28	71	1	4	<0.1	+	—
5	—	2.5	—	78	17	16	3	—	—
7	—	0.5	28	71	1	2	<0.1	+	—
8 (exploded)	0.5	24	3	—	70	195	7	—	—
old stock ^c	2	33	7	—	58	—	—	—	+

^aGLC analysis were performed on SCOT Ucon LB 550X columns, temperature programming 70–170°C, 1°/min. The gas chromatograph was coupled with a single focussing CH-7H Varian MAT mass spectrophotometer. Data are given as percentage of total peak area measurements and are only semi-quantitative.

^bMixture prepared in glass according to the plant procedure, ratio PC-DIPE is 55:45 by weight and 45:55 by volume.

^cRemainder of an earlier production, stored in the open for 8 months. It was vented once!

^dConcentrations are given in mg/l.

^e+ coated; — non-coated.

(3) The reaction depicted in Scheme 1 went to completion in drum 8, which exploded, and also in the unexploded old stock. In drum 8 the reaction velocity was obviously much higher.

(4) The reaction takes place in coated drums as well as in non-coated ones.

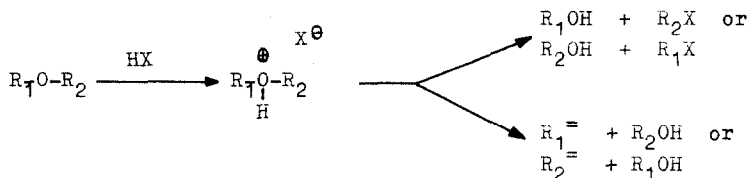
(5) The samples from all drums contain iron and zinc, the latter in a much lower concentration.

(6) There is no correlation between the amount of iron and the kind of drums. It seems, however, that coated drums contain significantly less zinc than non-coated ones. Drum 8 is not representative because the concentration of Fe and Zn would have been considerably increased due to evaporation of DIPE or isopropyl chloride (the contents were boiling).

It is well known that DIPE, like other ethers, is susceptible to autoxidation. The intermediate dihydroperoxide rearranges to the explosive acetone peroxide trimer, which was isolated and identified by Rieche and Koch (1942) and Acree and Haller (1943) from DIPE samples stored for several years. When ethers are used at Naarden, determination of the peroxide number is a standard procedure. This method proved the DIPE used to be peroxide free! The observed, rapid, quantitative conversion of the PC-DIPE mixture into isopropyl chloride and isopropyl propionate, by exothermic decomposition of peroxides, is therefore not only very unlikely, but also without precedence in the literature. Furthermore, no typical peroxide rearrangement products (e.g. acetone, formaldehyde and formic acid) were observed in the GLC-mass spectra. However, the observed phenomenon is wholly explained by the presence of low concentrations of heavy metals.

Chemistry

Dialkyl ethers are considered to be rather inert solvents. The C—O bond, with a bond energy of about 80 kcal, can only be broken under extreme conditions. This reaction can proceed via oxonium intermediates (Scheme 2).



Scheme 2

The velocity of the ether cleavage depends partly on the acid strength. For primary ethers the reactivity increases from HCl to HBr to HI, in a ratio of 1:6:∞ (Lüttringhaus and Saäf, 1938). As can be deduced from Scheme 2, the structures of the R₁ and R₂ groups also play an important role in the decomposition process. The ether is cleaved more readily with increasing ease of

formation of a carbenium ion from the oxonium salt (leading to RX and R⁼ formation). It is known for example that *t*-butyl methyl ether reacts very rapidly at room temperature with excess HCl, quantitatively giving *t*-butyl chloride (Norris and Wayne Rigby, 1932).

The stability of ethers as a function of their structures can also be illustrated by some second order thermodynamic calculations (Seaton et al., 1974) shown in Tables 2 and 3.

Table 2

Table 3

ΔH Kcal	ΔS Gibbs	ΔG Kcal	T K		ΔH Kcal	ΔS Gibbs	ΔG Kcal	T K
<chem>CCOC</chem> \longrightarrow <chem>CCO</chem> + <chem>C=C</chem>				A	<chem>CCOC</chem> \xrightarrow{HCl} <chem>CCO</chem> + <chem>CCl</chem>			
11.4 *		2.3	298 *		0.5	-7.0	-1.6	298
13.6 **			298		0.5	-6.0	-1.8	373
<chem>CC(C)OC</chem> \longrightarrow <chem>CC(C)O</chem> + <chem>C=C</chem>				B	<chem>CC(C)OC</chem> \xrightarrow{HCl} <chem>CC(C)O</chem> + <chem>CC(C)Cl</chem>			
17.4	40.1	5.5	298		-0.3	5.7	-2.0	298
16.7	38.5	-5.3	573		-1.2	3.8	-3.4	573
<chem>CC(C)(C)OC</chem> \longrightarrow <chem>CC(C)(C)O</chem> + <chem>C=C</chem>				C	<chem>CC(C)(C)OC</chem> \xrightarrow{HCl} <chem>CC(C)(C)O</chem> + <chem>CC(C)(C)Cl</chem>			
18.3	40.4	3.3	373		1.1	3.9	-0.1	298
17.5	38.6	-8.5	673		1.0	3.6	-0.4	373
<chem>CC(C)OC(C)C</chem> \longrightarrow <chem>CC(C)OC(C)C</chem> + <chem>C=C</chem>				D	<chem>CC(C)OC(C)C</chem> \xrightarrow{HCl} <chem>CC(C)OC(C)C</chem> + <chem>CC(C)Cl</chem>			
17.6	38.7	6.0	298		-0.2	3.0	-1.1	298
17.4	38.4	3.1	373		-1.0	1.1	-1.7	573

Notes: * Values according to Perry, 1963
 ** Value according to Hougen et al., 1943

From Table 2 we may conclude that the ethers considered are stable compounds, at least up to their boiling points. Their thermal, acid-catalysed decomposition into an alcohol and an alkene is endothermic (positive ΔH) and no spontaneous reaction will take place due to the positive ΔG . In fact, industrial ether synthesis takes place via the reverse reaction.

In the presence of equimolecular amounts of nucleophilic acids like HCl, the stability of the ethers is decreased. As can be seen from Table 3, their ΔG values are all negative, even at room temperatures. Ether cleavage will proceed spontaneously in all cases.

It must be stressed that these figures do not predict reaction velocity. This value is related to the activation energy ΔG^\ddagger , obtained from kinetic measurements, in which the catalyst and the temperature are two important variables.

In other words, the values of ΔH and ΔG for the formation or decomposition of a compound are only determined by the enthalpies and entropies of starting materials and end products, and not by the reaction mechanism of the formation or decomposition.

Although Lewis acids like ZnCl_2 can induce decomposition of ethers into alcohols and alkenes under extreme conditions, according to Underwood et al. (1930), this reaction has no preparative importance. Acid chlorides, as such, react very slowly with ethers (Houben-Weyl, 1965) and only the more reactive and unstable acid iodides react with ethers at room temperature (Justus and Stevens, 1933). Yet it can be shown that this combination is thermodynamically very unstable. This is illustrated by Table 4. It is obvious that reaction of an ether with an acid chloride can proceed spontaneously even at room temperature.

Table 4

ΔH Kcal	ΔS Gibbs	ΔG Kcal	T K
<chem>CCOC + CC(=O)Cl >> CC(=O)OC + CCl</chem>			
0.5	-7.0	-1.6	298
0.5	-6.0	-1.8	373
<chem>CCOC(C) + CC(=O)Cl >> CC(=O)OC(C) + CCl</chem>			
-10.3	3.1	-11.2	298
-7.5	9.7	-13.1	573
<chem>CCOC(C) + CC(=O)Cl >> CC(=O)OC(C) + C=C + HCl</chem>			
7.5	38.8	-4.1	298
10.4	45.8	-15.8	573

The reaction path via ester and alkyl chloride is most likely (with negative or very weak positive ΔH). The formation of an alkene (propene) can proceed as well, since the large positive ΔS contribution makes ΔG negative notwithstanding the large positive ΔH .

It is not surprising that this reaction is also accelerated by Lewis acids (Meerwein and Maier-Hüser, 1932; Thomas, 1941; Olah, 1965a). The most effective catalysts are ZnCl_2 (Varvoglis, 1937) and SnCl_4 (Burwell et al., 1951); sometimes FeCl_3 (Underwood and Wakefield, 1930) and sulphuric acid (Varvoglis, 1937) are mentioned.

The literature indicates that the reaction of ethers with acid chlorides to give esters and alkyl or aryl chlorides has preparative importance only when a substantial amount of catalyst (10–100 mol %) is used. This can be expected because complex formation of the Lewis acid with the carbonyl function does

not vanish along the reaction coordinate, although its character is altered (Meerwein and Maier-Hüser, 1932). This is why the Lewis-acid catalyst reactivity (Meerwein and Maier-Hüser, 1932; Olah, 1965a) is inverse to the activity sequence in aromatic acylation (Olah, 1965b):



From this sequence it is apparent that dimethyltoluidines can be acetylated under the influence of AlCl_3 in diethyl ether as the solvent (Thomas, 1941, p. 195), although Table 4 shows that this procedure may cause loss of valuable raw material by the formation of the very volatile ethyl chloride (B.P. 13°C).

It is my opinion that the lability of the ether—acid chloride system is largely underestimated in the literature. In contrast to the general concept of the need of large quantities of catalysts, only two examples have been found where the reaction was catalyzed by very small (~ 0.1 mol %) quantities (Burwell et al., 1951; Kyrides, 1933).

sec-Butyl methyl ether reacts with acetyl chloride in the presence of 0.1 mol % of SnCl_4 even at -80°C . The reaction is very rapid at 0°C , and runs out of hand without proper cooling. Without catalyst or in the presence of HCl , no reaction takes place. In conclusion we can say that even much lower concentrations of heavy metals catalyze the reaction effectively (Table 1) and might be responsible for the accident described above.

Conclusion

Mixtures of propionyl chloride with diisopropyl ether are very unstable. The exothermic reaction giving isopropyl propionate and isopropyl chloride has a ΔH_{25} of -10 kcal/mole and a ΔG_{25} of -11 kcal/mole, and can proceed spontaneously. This process is effectively catalyzed by extremely low concentrations of ZnCl_2 (4 ppm) or somewhat less effectively by FeCl_3 (40 ppm). In this way pressure may build up in closed vessels, with an explosion as the result. Thus premixing of ethers and acid chlorides should be avoided.

Acknowledgement

The full cooperation of plant management, staff and operators to obtain as many relevant samples as possible is gratefully acknowledged. I am also very grateful for the assistance of the Analytical Departments in running analyses without delay. I am very much indebted to Dr. H.G. Haring for the CHETAH calculations.

References

- Acree, F. (Jr.), and Haller, H.L., 1943. Trimolecular acetone peroxide in isopropyl ether. *J. Amer. Chem. Soc.*, 65: 1652.
- Burwell, R.L., Elkin, L.M., and Maury, L.G., 1951. Cleavage reactions of optically active secondary butyl methyl ether. *J. Amer. Chem. Soc.*, 73: 2428—2431.

- Breslow, D.S., Baumgarten, E., and Hauser, C.R., 1944. A new synthesis of β -keto esters of the type $\text{RCOCH}_2\text{COOC}_2\text{H}_5$. *J. Amer. Chem. Soc.*, 66: 1286–1288.
- Justus, E.L., and Stevens, P.G., 1933. Studies on acid iodides II. The cleavage of aliphatic ethers by acid iodides. *J. Amer. Chem. Soc.*, 55: 378–386.
- Houben, J. and Weyl, Th., 1965. *Methoden der Organische Chemie*, (4th edn.) Part 3, Georg Thieme Verlag, Stuttgart, pp. 155–157.
- Hougen, O.A., and Watson, K.M., 1943. *Chemical process principles*, John Wiley, New York, p. 262.
- Kyrides, L.P., 1933. The reaction between acid chlorides and ethers in the presence or zinc chloride, *J. Amer. Chem. Soc.*, 55: 1209–1212.
- Lund, H., 1934. Über Darstellung und synthetische Verwendung von Magnesiummalonester. *Ber.*, 67B: 935–938.
- Lüttringhaus, A., and Saäf, G. v., 1938. Methods for splitting phenol ethers. *Angew. Chemie*, 51: 916–920.
- Meerwein, H. and Maier-Hüser, H., 1932. Untersuchungen über Eigenschaftsänderungen chemischer Verbindungen durch Komplexbildung VII. Über den Mechanismus der Ätherspaltungen durch Säurechloride und Säureanhydride in Gegenwart von Katalysatoren. *J. Prakt. Chemie*, 134: 51–81.
- Norris, J.F., and Wayne Rigby, G., 1932. The reactivity of atoms and groups in organic compounds XII. The preparation and properties of mixed aliphatic ethers with special reference to those containing the tert.-butyl radical. *J. Amer. Chem. Soc.*, 54: 2088–2100.
- Olah, G.A., 1965a. *Friedel-Crafts and Related Reactions (Vol. IV)*, Interscience Publishers, pp. 12–20.
- Olah, G.A., 1965b. *Friedel-Crafts and Related Reactions (Vol. III)*, Interscience Publishers, p. 9.
- Perry, J.H., 1963. *Chemical Engineers' Handbook (4th edn.)*, Vol. 3, McGraw-Hill, New York, p. 135.
- Rieche, A., and Koch, K., 1942. Die Oxydation des Diisopropyläthers (XIV. Mittel. über Äthylperoxyde). *Ber.*, 75, 1016–1028.
- Seaton, W.H., Freedman, E., and Treweek, D.N., 1974. CHETAH — The ASTM chemical thermodynamic and energy release evaluation program, ASTM, Philadelphia.
- Thomas, C.A., 1941. *Anhydrous Aluminium Chloride in Organic Chemistry*, Rheinhold, New York.
- Underwood, H.W. (Jr.), and Baril, O.L., 1930. Catalysis in organic chemistry III. Decomposition of esters by anhydrous zinc chloride. *J. Amer. Chem. Soc.*, 52: 395–397.
- Underwood, H.W. (Jr.), and Toone, G.C., 1930. Catalysis in organic chemistry II. Mechanism of the reactions of ethers with acid chlorides, acids and anhydrides. *J. Amer. Chem. Soc.*, 52: 391–394.
- Underwood, H.W. (Jr.), and Wakefield, R.L., 1930. Catalysis in organic chemistry I. Reactions of ethers with acid chlorides, acids and anhydrides. *J. Amer. Chem. Soc.*, 52: 387–391.
- Varvoglis, G.A., 1937. Über die Einwirkung von Metallen auf Säurechloride. *Ber.*, 70: 2391–2396.