

LXXXV.—*The Temperature of Explosion for Endothermic Substances.*

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BERTHELOT has shown (*Compt. rend.*, 1887, 105, 1159; 1899, 129, 926) that certain endothermic substances which, if heated gradually, would either volatilise or decompose, can be made to explode by throwing them into a vessel previously raised to a suitably high temperature. This result was observed with trinitrophenol, mono-, di-, and tri-nitronaphthalene, and potassium chlorate. The authors, following up these observations of Berthelot, find that for each endothermic substance there is a temperature below which explosive decomposition does not occur, and this definite point is termed the temperature of explosion.

The procedure adopted was to drop a small quantity of the substance to the bottom of a clean test-tube immersed in a bath of potassium hydrogen sulphate just when the temperature of the bath has attained the temperature particular to each substance, as otherwise a simple decomposition would take place. The temperature of this bath, up to 500°, was recorded on a mercury thermometer; at higher temperatures, a thermo-couple was employed. The experiment was carried out in an atmosphere of carbon dioxide, but any other indifferent gas, such as nitrogen, may be used, and explosive decomposition occurs with equal readiness in a vacuum.

From the results recorded below for the temperatures of explosion of various substances, one or two conclusions of a general kind may be drawn. So far as nitro-derivatives are concerned, it appears that, of the disubstituted derivatives of benzene, the ortho-compound, as a rule, has the lowest, and the para-compound the highest, temperature of explosion. Thus the temperatures of explosion for *o*-, *m*-, and *p*-chloronitrobenzene are 614°, 638°, and

720° respectively. In the case, however, of the nitrophenols, the *para*-compound has a lower temperature of explosion than the *meta*-compound. For dinitro-compounds with the nitro-group in the *meta*-position, the temperature of explosion falls as the number of alkyl-groups attached to the ring increases. In this connexion, the figures for the temperatures of explosion of *m*-dinitrobenzene, 2:4-dinitrotoluene, and 4:6-dinitro-*o*-xylene may be quoted: they are 580°, 470°, and 438° respectively. The same relation holds good in the case of trinitro-derivatives.

In the following record, the temperature of explosion follows the name of the compound examined.

#### *Nitro-compounds.*

*o*-Dinitrobenzene, 472°; *m*-dinitrobenzene, 580°; 1:3:5-trinitrobenzene, 520°; 2:4-dinitrotoluene, 470°;  $\alpha$ -2:4:6-trinitrotoluene, 418°; 4:6-dinitro-*o*-xylene, 438°; 3:4-dinitro-*o*-xylene, 413°; trinitroxylene (m. p. 178°), 408°; 2:4:6-trinitro-*m*-xylene, 410—412°; 2:3:6-trinitro-*p*-xylene, 410°; dinitromesitylene, 418°; trinitromesitylene, 415°; trinitrocumene, 502°; 2:4-dinitrostilbene, 412°; *o*-dinitrostilbene, 420°;  $\alpha$ -dinitrodiphenylmethane (m. p. 181°), 335°; 1:6-dinitronaphthalene, 492°; 1:8-dinitronaphthalene, 445°; trinitronaphthalene (m. p. 122°), 364°; tetranitronaphthalene (m. p. 170°), 323°; *o*-chloronitrobenzene, 614°; *m*-chloronitrobenzene, 638°; *p*-chloronitrobenzene, 720°; *p*-bromonitrobenzene, 755°; *p*-iodonitrobenzene, 605°; *o*-nitroaniline, 655°; *m*-nitroaniline, 552°; *p*-nitroaniline, 627°; 2:4-dinitroaniline, 548°; *p*-nitrobenzoic acid, 635°; 2:4-dinitrobenzoic acid, 484°; 3:5-dinitrobenzoic acid, 523°; *o*-nitrophenol, 630°; *m*-nitrophenol, 657°; *p*-nitrophenol, 633°; 2:4-dinitrophenol, 498°; 2:4:6-trinitrophenol, 418°; 3-nitro-*o*-cresol, 503°; 6-nitro-*m*-cresol, 393°; 3:4-dinitro-*o*-cresol, 472°; 3:5-dinitro-*o*-cresol, 455°; 2:4:6-trinitro-*m*-cresol, 405°; 5-nitro-*p*-xylenol, 407°; 3:5-dinitro-*o*-xylenol, 432°; 2:4:6-trinitroresorcinol, 314°; *o*-dinitrodihydroxydiphenyl (m. p. 184°), 447°; 2:6-dichloro-4-nitrophenol, 548°; 4:6-dichloro-2-nitrophenol, 562°; 2:6-dibromo-4-nitrophenol, 625°; 4:6-dibromo-2-nitrophenol, 630°; 2:4:6-tribromo-3-nitrophenol, 605°; 6-bromo-2:4-dinitrophenol, 713°; 2-iodo-3-nitrophenol, 448°; 2:4-di-iodo-6-nitrophenol, 533°; 2:6-di-iodo-4-nitrophenol, 548°.

#### *Picrates.*

Ammonium picrate, 423°; hydrazine picrate, 385°; allylamine picrate, 270°; carbamide picrate, 489°; semicarbazide picrate,

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474°; guanidine picrate, 498°; hexamethylenetetramine picrate, 360°; aniline picrate, 398°; *o*-toluidine picrate, 400°;  $\alpha$ -naphthol picrate, 458°;  $\beta$ -naphthol picrate, 469°; naphthalene picrate, 484°; phenanthrene picrate, 478°; acenaphthene picrate, 418°; pyridine picrate, 432°; quinine picrate, 280°; quinidine picrate, 272°; cinchonine picrate, 268°; cinchonidine picrate, 260°; strychnine picrate, 290°; atropine picrate, 460°.

*Azo-compounds.*

Azobenzene, 540°; aminoazobenzene, 598°; dimethylaminoazobenzene, 643°; diazoaminobenzene, 703°.

*Haloid Compounds.*

Iodoform, 295°; *p*-di-iodobenzene, 788°; 2:4:6-tri-iodophenol, 675°; di-iodo-*o*-cresol, 782°; 2:4:6-tri-iodo-*m*-cresol, 696°; 2:4:6-tribromoresorcinol, 713°; 2:4:6-tribromo-*o*-rcinol, 793°; penta-bromo-*o*-rcinol, 698°.

*Organic Perchlorates.*

Allylamine perchlorate, 262°; methylamine perchlorate, 338°; propylamine perchlorate, 290°; heptylamine perchlorate, 265°; hexylamine perchlorate, 278°; aniline perchlorate, 250°.

*o*-Toluidine perchlorate.—This salt has not previously been described. It is prepared by neutralising the base with perchloric acid. It does not melt on heating, but slowly carbonises:

0.0993 gave 6 c.c.  $N_2$  at 28° and 760 mm.  $N=6.72$ .

$C_7H_9N, HClO_4$  requires  $N=6.76$  per cent.

It explodes at 260°.

*m*-Toluidine perchlorate.—This salt was prepared by the interaction of the hydrochloride of the base and silver perchlorate. It melts and chars at 200°:

0.0804 gave 4.9 c.c.  $N_2$  at 28° and 760 mm.  $N=6.78$ .

$C_7H_9N, HClO_4$  requires  $N=6.76$  per cent.

It explodes at 300°.

The following perchlorates were prepared by double decomposition, as in the preceding case.

*p*-Toluidine perchlorate:

0.1027 gave 6.2 c.c.  $N_2$  at 29° and 760 mm.  $N=6.70$ .

$C_7H_9N, HClO_4$  requires  $N=6.76$  per cent.

It explodes at 278°.

*m*-4-*Xylylidine perchlorate* decomposes at 200°:

0·1000 gave 5·8 c.c. N<sub>2</sub> at 28° and 760 mm. N=6·45.

C<sub>8</sub>H<sub>11</sub>N, HClO<sub>4</sub> requires N=6·33 per cent.

It explodes at 260°.

*p*-*Xylylidine perchlorate* decomposes at 210°:

0·1072 gave 6 c.c. N<sub>2</sub> at 28° and 760 mm. N=6·33.

C<sub>8</sub>H<sub>11</sub>N, HClO<sub>4</sub> requires N=6·33 per cent.

It explodes at 258°.

*Benzylamine perchlorate* melts at 120°:

0·0816 gave 5·2 c.c. N<sub>2</sub> at 28° and 760 mm. N=7·09.

C<sub>7</sub>H<sub>9</sub>N, HClO<sub>4</sub> requires N=6·76 per cent.

It explodes at 305°.

Phenylethylamine perchlorate, 280°;  $\alpha$ -naphthylamine perchlorate, 228°; menthylamine perchlorate, 308°.

*Camphylamine perchlorate* melts and decomposes at 215°:

0·0570 gave 3·1 c.c. N<sub>2</sub> at 29° and 760 mm. N=5·97.

C<sub>10</sub>H<sub>19</sub>N, HClO<sub>4</sub> requires N=5·53 per cent.

It explodes at 255°.

*Diethylamine perchlorate* melts at 107° and is very hygroscopic:

0·1067 gave 7·8 c.c. N<sub>2</sub> at 28° and 760 mm. N=8·13.

C<sub>4</sub>H<sub>11</sub>N, HClO<sub>4</sub> requires N=8·09 per cent.

It explodes at 282°.

Dipropylamine perchlorate, 308°; diamylamine perchlorate, 323°; benzylethylamine perchlorate, 322°; benzylmethylamine perchlorate, 294°.

*Dibenzylamine perchlorate* explodes at 290°:

0·0574 gave 2·6 c.c. N<sub>2</sub> at 27° and 760 mm. N=5·31.

C<sub>14</sub>H<sub>15</sub>N, HClO<sub>4</sub> requires N=4·7 per cent.

*p*-*Tolyltrimethylammonium perchlorate* melts at 192°:

0·0670 gave 3·8 c.c. N<sub>2</sub> at 30° and 760 mm. N=6·08.

C<sub>10</sub>H<sub>16</sub>N, ClO<sub>4</sub> requires N=5·62 per cent.

It explodes at 310°.

*Methylpyridinium perchlorate* explodes at 362°:

0·0661 gave 4·9 c.c. N<sub>2</sub> at 32° and 760 mm. N=8·12.

C<sub>6</sub>H<sub>9</sub>N, ClO<sub>4</sub> requires N=7·61 per cent.

*Ethylpyridinium perchlorate* explodes at 340°:

0·0765 gave 4·9 c.c. N<sub>2</sub> at 30° and 760 mm. N=7·07.

C<sub>7</sub>H<sub>11</sub>N, ClO<sub>4</sub> requires N=6·73 per cent.

Neurine perchlorate, 298°; phenylbenzylmethylammonium perchlorate, 275°; trimethylsulphonium perchlorate, 280°; ethylquinolinium perchlorate, 330°; propylquinolinium perchlorate,

342°; ethylquinaldinium perchlorate, 268°; hydrazine monoperochlorate, 238°; hydrazine diperochlorate, 215°; trimethylenediamine perchlorate, 310°; ethylenediamine perchlorate, 270°.

*Guanidine perchlorate* melts at 237°:

0.2249 gave 53 c.c. N<sub>2</sub> at 29° and 760 mm. N=26.15.

CH<sub>5</sub>N<sub>3</sub>,HClO<sub>4</sub> requires N=26.41 per cent.

It explodes at 367°.

*Semicarbazide perchlorate* explodes at 278°:

0.0929 gave 20.2 c.c. N<sub>2</sub> at 30° and 760 mm. N=24.01.

CH<sub>5</sub>ON<sub>3</sub>,HClO<sub>4</sub> requires N=24.00 per cent.

*Piperazine perchlorate* melts at 80°:

0.1156 gave 9 c.c. N<sub>2</sub> at 29° and 760 mm. N=8.64.

C<sub>4</sub>H<sub>10</sub>N<sub>2</sub>,2HClO<sub>4</sub>,2H<sub>2</sub>O requires N=8.69 per cent.

It explodes at 290°.

*o*-Phenylenediamine perchlorate explodes at 250°:

0.0310 gave 2.6 c.c. N<sub>2</sub> at 27° and 760 mm. N=9.31.

C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>,2HClO<sub>4</sub> requires N=9.09 per cent.

*m*-Phenylenediamine perchlorate, 263°; *p*-phenylenediamine perchlorate, 260°.

#### *Alkaloids, etc.*

Brucine, 793°; narcotine, 720°; narceine, 697°; chloralurethane, 673°; oxalyhydrazide, 548°; acetophenoneoxime, 734°; benzil, 643°.

Investigations on similar lines are being continued.

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