Studies on the Linear Crystallization of TNT Systems[1]

BY W. A. GEY, E. R. DALBEY AND R. W. VAN DOLAH

An extensive study has been made of the role of additives in influencing the linear crystallization rate of TNT. Crystallization rates were determined for mixtures of TNT with over forty compounds ranging from 2,4-dinitrotoluene and 2-naphthol to a long series of substituted stilbenes. 2,4,6-Trinitrostilbene and its derivatives were found to be extremely effective in lowering the crystallization rate. The behavior of the additives has been considered in terms of adsorption theory and two adsorption isotherm equations have been derived. The simpler considers only the reversible processes, while the second, to account for the exteme rate-reducing effectiveness of certain additives, considers an irreversible adsorption process as well. The relative activities of a large number of compounds were studied in relation to their structures. The trinitrophenyl group uniformly conferred strong rate-reducing effects. An ethylene bridge to the remainder of the molecule created more effective additive molecules than the other linkages studied.

Prior to a recent publication[2] dealing with factors influencing the crystallization velocity of TNT this Laboratory had completed an extensive investigation in this field as part of a continuing interest in the physical properties and behavior of this compound.

Many studies were made of the crystallization of organic and inorganic substances in capillary tubes in the 1890–1915 period. This work has been summarized by Freundlich,[3] who was the first to point out that the retardation of linear crystallization of compounds by additives was probably due to adsorption of the foreign substance on the growing face. He demonstrated that the relation between the rate of linear crystallization R and the concentration of the additive C could be expressed, for most compounds, by the equation

$$\frac{R_0 - R}{R_0} = kC^{1/n}$$

in which the quantity $(R_0 - R)/R_0$ is a measure of the adsorption, R_0 being the rate for the pure substance. This relation was shown to hold over a wide range of concentrations, with values for $1/n$ of 0.2 to 0.7. He also showed that the values so obtained were relatively the same as those obtained by adsorbing the substances from solution upon activated charcoal.[4]

The necessary specificity of additives indicated by Freundlich's theory is in abrupt disagreement with the slightly earlier work of Von Pickardt,[5] who concluded the retardation of crystallization velocity to be a colligative property, being proportional to the square root of the concentration, thus allowing its use in deriving molecular weight.

Comparatively little use of this technique has been made in recent years, although McCrone and co-workers[6] have applied linear crystallization rates to the estimation of purity of p,p'-DDT, attributing the action of the impurity to changes in viscosity; however, such mixtures contained large quantities (20%) of impurity. In the work reported

herein, additional evidence has been accumulated to support the adsorption concept, at least in the cases involving low concentration of added or adventitious materials.

Experimental

Dinitro- and Trinitrotoluenes.—Commercial grade 2,4,6-trinitrotoluene (TNT) was purified for the earlier studies by two or three recrystallizations from 95% ethanol, m.p. 80.9–81.4°.[7] Later it was found that the purity of the material could be improved greatly by a more involved procedure. This consisted of adding a solution of 1 part TNT in 2 parts of acetone to 15 parts of cold water, filtering, washing solvent-free, and stirring the TNT with 5 parts of 8% sodium sulfite solution at 50–60° for 10 minutes. After filtering and washing with cold water until the effluent was colorless, the air-dried product was dissolved in 5 parts of hot carbon tetrachloride and the solution washed with warm water until the washings were colorless. The TNT, recovered by cooling and filtering, was then recrystallized from 95% ethanol and carefully dried over sulfuric acid. Recoveries were 75% of the starting material and melted at 81.5°.

2,4,5-Trinitrotoluene.[8]—To a solution of 25 ml. of nitric acid (sp. gr. 1.42) in 40 ml. of fuming sulfuric acid was added slowly 7.0 g. (0.038 mole) of 3,4-dinitrotoluene. The solution was heated for 23 hours on a steam-bath, cooled and drowned into 500 ml. of ice-water. The precipitate was filtered, washed acid free, and added to 30 ml. of boiling ethanol. After cooling, 5.4 g. (61.7%) of dry product melting at 104–105° was obtained. The 3,4-dinitrotoluene[9] was prepared from 3-nitro-4-aminotoluene.[10]

2,4-Dinitrotoluene.—2,4-Dinitrotoluene (Eastman Kodak) was purified by several recrystallizations from absolute methanol and dried in a vacuum over sulfuric acid.

Nitrostilbenes.—The following, previously reported, nitrostilbenes were prepared: 2,4,6-trinitrostilbene,[11] m.p. 157–158°; 2,4,4',6-tetranitrostilbene,[11] m.p. 195–196°; 2,3',4,6-tetranitrostilbene,[12] m.p. 160–160.5°; 2,4,6-trinitro-4'-methoxystilbene,[13] m.p. 166.5–167.5°; 2,4,4'-trinitrostilbene,[13] m.p. 239.5–240°; 2,3',4-trinitrostilbene,[14] m.p. 181–182° (uncor.); 2,4-dinitrostilbene,[14] m.p. 138–139° (uncor.); 2,4-dinitro-4'-dimethylaminostilbene,[13] m.p. 181–182°.

Additional nitrostilbenes (Table I), previously unreported in the literature were prepared by the usual method of condensing substituted aromatic aldehydes with 2,4,6-trinitrotoluene.[14]

Other Nitroaromatics.—The following previously reported nitroaromatic compounds were prepared: 1,3-bis-(2,4,6-trinitrophenyl)-2-phenylpropane,[15] m.p. 186–187°; 2,4,6-trinitrodiphenyl ether,[16] m.p. 154–155°; 2,4,6-tri-

(1) Presented in part at the 124th Meeting of the American Chemical Society, Chicago, September, 1953.

(2) Z. Pelchowicz and E. D. Bergmann, *Bull. Research Council Israel*, 1, 134 (1951).

(3) H. Freundlich, "Colloid and Capillary Chemistry," Methuen and Co., Ltd., London, 1926.

(4) H. Freundlich, *Z. physik. Chem.*, 75, 245 (1910).

(5) E. Von Pickardt, *ibid.*, 42, 17 (1903).

(6) (a) W. A. McCrone, A. Smedal and V. Gilpin, *Ind. Eng. Chem., Anal. Ed.*, 18, 578 (1946); (b) V. Gilpin, W. A. McCrone, A. Smedal and H. Grant, THIS JOURNAL, 70, 208 (1948).

(7) All melting points were determined in capillary tubes and are corrected unless otherwise noted.

(8) Directions given by W. Will, *Ber.*, 47, 704 (1914), are not specific, so the conditions used are given.

(9) H. J. Page and B. R. Heasman, *J. Chem. Soc.*, 123, 3241 (1923).

(10) L. Gattermann, *Ber.*, 18, 1483 (1885).

(11) G. Ullmann, *ibid.*, 41, 2291 (1908).

(12) G. Bishop and O. Brady, *J. Chem. Soc.*, 121, 2364 (1922).

(13) H. B. Nisbet, *ibid.*, 2081 (1927).

(14) E. Thiele, *Ber.*, 34, 2843 (1901).

(15) A. Postak, *Bull. soc. chim.*, 39, 77 (1926).

(16) C. Willgerodt, *Ber.*, 12, 1278 (1879).

TABLE I

CHARACTERIZATION OF NEW POLYNITROSTILBENES

Compound	Color	M.p., °C.	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found	Halogen, % Calcd.	Found
p-Di-(2,4,6-trinitrophenylethenyl)-benzene	Orange-yellow	300	47.83	47.82	2.35	2.24	15.22	15.42		
3'-Iodo-2,4,6-trinitrostilbene	Greenish yellow	156–156.5	38.11	38.37	1.83	2.03	9.53	9.68	28.77	29.57
4'-Phenyl-2,4,6-trinitrostilbene	Orange	223–223.5	61.38	61.40	3.35	3.41	10.74	10.53		
2'-Chloro-2,4,6-trinitrostilbene	Greenish yellow	145.5–146.0	48.08	48.16	2.31	2.29	12.02	12.28	10.14	10.83
4'-Hydroxy-2,4,6-trinitrostilbene	Bright red	219–220	50.76	50.74	2.74	2.87	12.69	12.66		
2'-Methoxy-2,4,6-trinitrostilbene	Reddish orange	151.5–152.0	52.18	52.35	3.21	3.25	12.17	12.56		
2',4'-Dichloro-2,4-dinitrostilbene	Orange	216.0–216.5	49.58	49.78	2.38	2.43	8.26	8.58	20.91	20.82
2'-Hydroxy-2,4-dinitrostilbene	Bright yellow	192.5–193.5	58.72	59.19	3.52	3.70	9.79	9.84		
3'-Methyl-2,4-dinitrostilbene	Bright yellow	145–147	63.37	64.17	4.26	4.39	9.86	10.42		
4'-Phenyl-2,4-dinitrostilbene	Bright yellow	178–179	69.35	69.74	4.07	4.23	8.09	8.10		
4'-Isopropyl-2,4-dinitrostilbene	Bright yellow	179–179.5	65.37	65.38	5.16	5.14	8.97	9.00		

TABLE II

CHARACTERIZATION OF NEW NITROAROMATIC COMPOUNDS

Compound	Color	M.p., °C.	Yield, %	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found
N-Cetylpicramide	Yellow	85–85.5	77	58.40	58.60	7.97	7.88	12.39	12.32
1-Phenoxy-2-(2,4,6-trinitrophenoxy)-ethane	Tan	114–115	32	48.11	48.15	3.18	3.16	12.09	11.54
1-Phenoxy-2-(2,4,6-trintrophenoxy)-propane	Tan	118–119.5	49	49.57	50.52	3.61	4.22	11.57	11.74
2,4,6-Trinitrodiphenyl sulfide	Yellow	122–123		44.86	45.14	2.20	2.31	13.08	14.84
2,4,6-Trinitrophenyl-n-butyl ether	White	37–38	57.7	42.10	42.44	3.89	3.85	14.73	14.69
2,4,6-Trinitrophenyl-n-hexyl ether	White	32.5–34	44					13.42	14.34
2-Phenoxyethyl 3,5-dinitrobenzoate	White	73.6–75							

nitrophenetole,[17] m.p. 76.9–78°; benzaldehyde-2,4-dinitrophenylhydrazone,[18] m.p. 240.5–241°; 2,4,6-trinitrohydrazobenzene,[19] m.p. 179–180° dec.; 2,4,6-trinitroazobenzene,[19] m.p. 143–144°. New nitroaromatic compounds prepared are listed in Table II; detailed examples follow.

N-Cetylpicramide.—A solution of 2.0 g. of picryl chloride and 2.0 g. of hexadecylamine (Armeen 16D) in 20 ml. of benzene was refluxed for 30 minutes, cooled, and washed with 10 ml. of 10% sodium carbonate solution; the benzene was then evaporated. After one recrystallization from 50 ml. of alcohol, the yield of material, melting at 76.2–77.8°, was 2.8 g. (77% based on picryl chloride). Several crystallizations from benzene raised the melting point to 85–85.5°.

The ethers were prepared by reaction of picryl chloride with the sodium alcoholate, according to the procedure of Willgerodt,[18] or by nitration of the alkyl phenyl ether with mixed acid at 55° for 3 hours. The 2,4,6-trinitrodiphenyl sulfide was prepared from picryl chloride and thiophenol according to the procedure of Bogert and Evans.[20]

Miscellaneous.—2-Naphthol was J. T. Baker resublimed; anthracene (m.p. 217.7°) was J. T. Baker product recrystallized from benzene. The following were prepared as described in the references: terephthaldehyde,[21] m.p. 114–116°; 2,4,6-trinitro-1,3-xylene, m.p. 181.5–182.2°, by nitration of 1,3-xylene; 2-nitronaphthalene,[22] m.p. 78–79°; diphenyl-4-aldehyde,[23] m.p. 57–59°.

trans-Stilbene and mesitylene were Eastman Kodak Co. White Label grade; 2-phenoxyethanol (Dowanol No. 1) and 1-phenoxypropanol-2 (Dowanol No. 2) were obtained from Dow Chemical Co.; 2,2-dinitropropane, m.p. 53°, was obtained from Commercial Solvents; commercial RDX was recrystallized from acetone, m.p. 198.5–200.0°, 2-nitrothianaphthene and 2,4-dinitrothianaphthene were obtained from the Jefferson Chemical Company.

Rate of Linear Crystallization.—The apparatus used, essentially that of Freundlich,[4] consisted of a 2-mm. capillary U-tube to which had been sealed a section of 25 mm. tubing for receiving the sample and mixing. The horizontal center section was etched at 1-cm. intervals to provide fiducial points for the rate measurements.

TNT solutions were prepared by the addition of an accu-

rately weighed quantity of additive to a weighed amount (1 g.) of TNT in the large bulb of the equipment, melting in a bath at 90–95°, and mixed by bubbling air through the mixture from the capillary end. Starting with 0.25% by weight, the points of the LCV-concentration of additive curve were usually run at 0.5, 1.0, 2.0 and 3.0% on the same solution by adding the required increments and then remelting and mixing as before.

An alternative procedure, used for the preparation of extremely dilute solutions, was to weigh the TNT and additive into a weighing bottle, using 3 g. of TNT and 1% of additive, and melt at 95–100°, in an oven with periodic mixing to dissolve the additive. Portions of this solution were then diluted with weighed amounts of TNT to obtain the smaller concentrations.

To carry out the measurements, the TNT or TNT system was melted by suspending the tube in a bath held at 90–95°, then the tube was placed in a constant temperature bath maintained at the desired temperature below the melting point. Thermal equilibrium was usually attained within 3 minutes (allowing up to 30 minutes for thermal equilibrium caused no significant change in values), after which the TNT surface was touched with a fine copper or iron wire, initiating crystallization. The time required for the advancing crystal front to travel 5 cm. between marks on the horizontal section was measured with a stopwatch to the nearest 1/10th second. Three measurements of the linear crystallization velocity (LCV), which usually varied less than 1%, were used to obtain the reported values. In the crystallization of pure TNT the variation was often more than this, due to the characteristics of crystallization, and 5 to 10 readings were required to obtain averaged values, reproducible to ±2%. The crystallizing front for pure TNT was often almost invisible in ordinary light, but could readily be observed by the use of crossed polaroid filters. The measurement of the LCV of solutions which crystallized very slowly was made by observations with a cathetometer on the vertical arm of the U-tube, measuring accurately the time required for crystallization of 1 cm.

The effect of purification of TNT on its LCV at 74° was thoroughly investigated. Technical TNT crystallized at a rate of 1.56 cm./min. while the most highly purified materials crystallized at rates varying from 2.50 to 2.79 cm./min. and one purified and sublimed sample gave a rate of 3.10 cm./min.[24] It was found that while these variations were significant in the case of pure TNT, the effect on the rates obtained with deliberate mixtures of TNT and additive was quite small. Thus, though the LCV's of the samples of

(17) P. T. Austen, *Ber.*, **8**, 666 (1875).

(18) See reference 19, p. 229.

(19) E. Fisher, *Ann.*, 132 (1878).

(20) M. T. Bogert and R. L. Evans, *Ind. Eng. Chem.*, **18**, 301 (1926).

(21) J. N. Snell and A. Weissberger, *Org. Syntheses*, **20**, 92 (1940).

(22) W. J. Hickinbottom, "Reactions of Organic Compounds," 2nd Edition, Longmans, Green and Co., London, 1948, p. 380.

(23) D. H. Hey, *J. Chem. Soc.*, 2476 (1931).

(24) A. N. Campbell and E. J. Pritchard, *Can. J. Research*, **25B**, 183 (1947), report on LCV for TNT at 70° of 3.5 cm./min.

TNT used varied from the extremes of 1.81 cm./min. to 2.79 cm./min. at 74°, the LCV's of both, with 2% 2,4,6-trinitrostilbene added, were almost identical. Most of the measurements reported herein were made on TNT which had an LCV of 2.50 cm./min.

Phase Diagrams.—Utilizing the thaw–melt method, melting point diagrams were determined for systems containing three of the additives that were investigated. All showed, within the limits of accuracy of the method, only simple eutectics with no evidence of solid solution. Table III gives the results obtained. Calculation of the expected freezing point depression of TNT by the addition of 5 moles of each to 95 moles of TNT, using the cryoscopic constant of 11.5°, gives excellent agreement with the observed data, indicating the absence of abnormality in the solutions.

TABLE III
EUTECTICS WITH TRINITROTOLUENE

Component B	Eutectic temp.	Eutectic compn., mole % component B
1-Phenoxy-2-(2,4,6-trinitrophenoxy)-ethane	67	25
2,4,6-Trinitrostilbene	75	13
2,3',4,6-Tetranitrostilbene	77	8

Viscometry.—The equipment used was a Cannon–Fenske modified Ostwald viscometer, size 200, calibrated according to the ASTM method using a Bureau of Standards oil sample K5.

For conversion to absolute viscosity, the density–temperature relation was determined using a pycnometer of the self-filling type calibrated with freshly boiled distilled water at 79 and 91.35°. Table IV shows the density-temperature data for air-saturated liquid TNT.

TABLE IV
DENSITY OF LIQUID AIR-SATURATED TNT

Temp., °C.	72.3	79.2	86.2	92.4
Density, g./cc.	1.4718	1.4652	1.4588	1.4528

Figure 1 shows the relation of log absolute viscosity versus $1/T$ for pure TNT and includes points determined for solutions of several additives in pure TNT. The coincidence of the values determined for solutions of the crystal growth-active substances with those for pure TNT indicate that the viscosity of the solution is not significantly different.
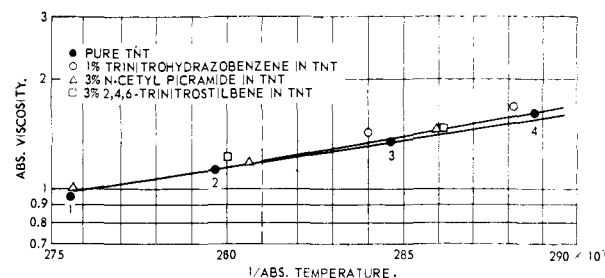
Fig. 1.—Variation of viscosity of liquid TNT with temperature.

Surface Tension.—The surface tensions of TNT and several TNT systems were determined by the Sugden–Quayle[25] maximum bubble-pressure method.

The radius of the capillary (0.1095 cm.) was measured with an optical comparator and the pressures were measured by a water-filled manometer. The apparatus was calibrated at 20° using benzene which had been carefully purified by partial freezing and fractional distillation.

At 81° the value obtained for pure TNT was 46.72 dynes/cm. N-Cetylpicramide, 2,4,6-trinitrophenyl glyceryl ether, 2-phenoxyethanol and 2,4,6-trinitrostilbene when added in amounts up to 2% had only negligible effects on the surface tension.

(25) O. R. Quayle and K. O. Smart, THIS JOURNAL, **66**, 937 (1944).

Discussion

For convenience of presentation, the data obtained on the linear crystallization velocity of TNT systems were plotted and interpolated values at uniform concentrations are given in Tables V and VI. All of the compounds studied could be grouped into three general classes typified by the three curves in which actual data are plotted, shown in Fig. 2. Curve A, representing the effect of 2,2-dinitropropane, is a straight line and could be caused by mere dilution effects, though our understanding of the mechanics of crystallization is inadequate to
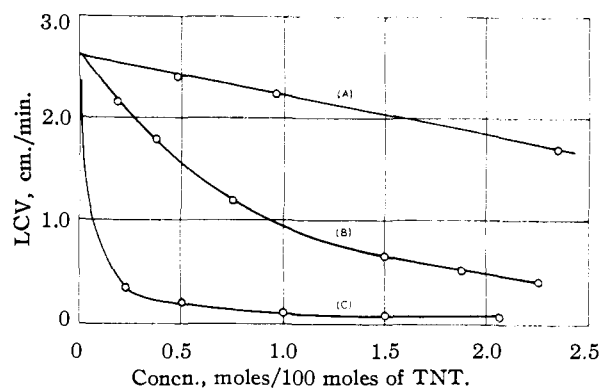
Fig. 2.—Effect of various classes of additives on the LCV of TNT at 74.0°: (A) class 1, e.g., 2,2-dinitropropane; (B) class 2, e.g., 2,4,6-trinitrodiphenyl ether; and (C) class 3, e.g., 2'-chloro-2,4,6-trinitrostilbene.
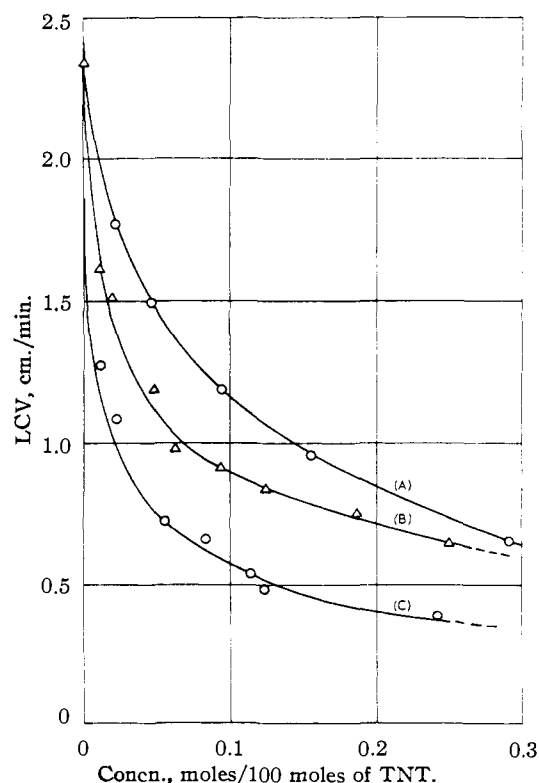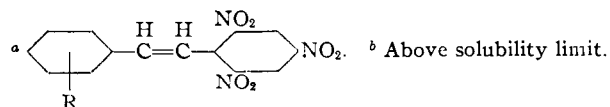
Fig. 3.—Effect of very small concentrations of additives on the LCV of TNT at 74.0°: (A) p-di-(β-trinitrophenylethenyl)-benzene; (B) 2,4,6-trinitrostilbene; (C) 3'-iodo-2,4,6-trinitrostilbene.

TABLE V

LINEAR VELOCITY OF CRYSTALLIZATION OF TNT AT 74.0° IN THE PRESENCE OF ADDITIVES

All values in cm./min.

Additive	0	0.25	0.5	1.0	1.5	2.0	2.5	3.0	3.5
Additives having little effect									
2,4-Dinitrotoluene	2.5	..	2.10	1.89	1.70	1.52	1.32	1.19	..
2,4,6-Trinitro-1,3-xylene	..	..	2.28	1.97	1.79	1.65	..	..	..
2,4,5-Trinitrotoluene	..	..	2.06	1.68	1.38	1.11	..	..	..
trans-Stilbene	..	..	2.32	2.09	1.88	1.65	..	..	..
2-Nitronaphthalene	..	2.65	2.51	2.25	2.00	..	..	..	..
2,2-Dinitropropane	..	..	2.43	2.24	2.04	1.86	1.68	..	..
Terephthaldehyde	..	2.58	2.49	2.31	..	..	..	..	..
2-Phenoxyethanol	..	..	1.73	1.62	1.50	1.35	1.11	..	..
2-Naphthol	..	..	2.08	1.84	1.60	1.39	..	1.10	..
RDX (Cyclotrimethylenetrinitramine)	..	2.20	2.05	1.78	1.57	1.36	..	..	..
2-Nitrothianaphthene	..	..	2.12	1.85	1.58	1.33	..	..	..
Mesitylene	2.79	2.70	2.64	2.50	2.35	2.20	2.05	1.89	1.78
Additives having intermediate effect									
2,4,6-Trinitrophenyl glyceryl ether	2.5	..	1.81	1.47	1.16	0.91	..	..	..
2,4,6-Trinitrophenyl n-hexyl ether	..	2.16	1.96	1.54	1.17	0.92	..	..	..
2,4,6-Trinitrodiphenyl ether	..	2.04	1.57	0.97	0.66	0.49	..	..	..
2,4,6-Trinitrophenyl n-butyl ether	..	..	2.07	1.67	1.35	1.09	..	..	..
2,4,6-Trinitrophenetole	..	..	1.65	1.37	1.13	0.91	0.75	..	..
N-Cetylpicramide	..	1.73	1.42	1.09	0.80	..	..	..	..
1-Phenoxy-2-(2,4,6-trinitrophenoxy)-propane	..	1.38	1.12	0.88	0.73	..	..	..	..
2,4,6-Trinitroazobenzene	..	1.33	1.07	0.76	0.59	0.48	..	..	..
2,4,6-Trinitrohydrazobenzene	..	1.06	0.81	0.57	0.44	0.35	..	..	..
2,4-Dinitrostilbene	..	1.57	1.23	0.91	0.72	..	..	..	..
2-Phenoxyethyl 3,5-dinitrobenzoate	..	1.68	1.31	0.95	0.77	0.63			
2,4,4'-Trinitrostilbene	2.5	1.49	1.19	0.86	0.61	0.47	..	..	..
2,4,3'-Trinitrostilbene	..	1.29	1.02	0.69	0.54	0.44	..	..	..
2,4-Dinitro-4'-dimethylaminostilbene	..	1.57	1.32	..	..	..	..	..	..
Additives having extreme effect, 2,4,6-Trinitro-stilbenes, where R^a is									
H	2.5	0.60	0.39	0.29	0.21	0.16	0.12	..	..
3'-Nitro	2.5	0.45	0.31	0.20	0.16	0.14	..	..	..
4'-Nitro	2.5	0.51	0.33	0.20	0.16	..	..	..	..
4'-Phenyl	2.5	1.08	0.72	0.43	0.29	0.22	0.16	..	..
2'-Chloro	2.5	0.32	0.20	0.12	0.08	0.06	..	..	..
2'-Methoxy	2.5	0.55	0.37	0.24	0.17	0.13	..	..	..
4'-Methoxy	2.5	0.55	0.38	0.25	0.18	..	..	..	..
4'-Hydroxy	2.5	0.40	0.30	0.19	0.15	..	..	..	..
3'-Iodo	2.5	0.38	0.27	0.17	0.12	0.09	..	..	..
Benzaldehyde 2,4-dinitrophenylhydrazone	..	0.83	0.60	0.39	0.30	0.27	..	..	..
p-Di-(2,4,6-trinitrophenylethenyl)-benzene	..	0.73	0.40	^{b}	..	..	..	..	..
1,3-Bis-(2,4,6-trinitrophenyl)-2-phenylpropane	..	1.00	0.78	0.55	0.40	0.30	..	..	..
1-Phenoxy-2-(2,4,6-trinitrophenoxy)-ethane	..	0 61	0.39	0.26	0.20	0.15	..	..	..

a [structure: 2,4,6-trinitrostilbene with R substituent] b Above solubility limit.

insist on this concept. Curve B, that of 2,4,6-trinitrodiphenyl ether, is more typical of the effects observed by Freundlich, namely, moderate reduction of crystallization velocity with a decrease in effectiveness with increasing concentrations. Curve C illustrates the extreme tendency to retard linear crystallization associated with trinitrostilbenes, the particular data being for 2-chloro-2,4,6-trinitrostilbene. This extreme effect led to an examination of several such compounds at high dilution, obtaining the data presented in Fig. 3. These demonstrate the sharp reduction in crystallization velocity which is effected by small amounts of certain compounds.

Effect of Structure.—With the wide variety of compounds studied it is of interest to compare their relative abilities to effect rate reduction with their structure. Immediately one is struck by the magnitude of growth activity conferred by the trinitrophenyl group. This is in confirmation of the results reported by Pelchowicz and Bergmann[1] who studied the effect of a series of esters containing this group. Unfortunately an accurate comparison with that work is not possible since those authors reported only the effect of concentration in each case and that at 60°. Only the limited amount of data given in Table VI was obtained in this work

TABLE VI

LINEAR VELOCITY OF CRYSTALLIZATION OF TNT IN THE PRESENCE OF ADDITIVES AT LOWER TEMPERATURES
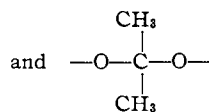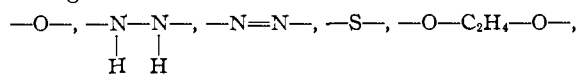
All values in cm./min.

Additive	Temp., °C.	Concentration of additive, moles/100 moles TNT							
		0	0.25	0.5	1.0	1.5	2.0	2.5	3.0
Mesitylene	68	9.62	8.75	8.25	7.60	7.10	6.65	6.32	6.02
2,4,6-Trinitrodiphenyl sulfide	67.6	9.42	5.65	4.25	3.00	2.42	2.00	1.70	1.42
2,4,6-Trinitrohydrazobenzene	67.6	9.32	..	1.86	1.11	0.82	..	..	..
2,4,4'-Trinitrostilbene	67.6	9.55	..	3.11	2.23	1.70	..	1.07	..
1-Phenoxy-2-(2,4,6-trinitrophenoxy)-ethane	67.6	9.46	..	1.40	0.90	0.60	0.44	0.32	0.23
2,4,6-Trinitrostilbene	63.8	12.20	2.93	1.82	1.15	0.80	0.58	..	..
	67	9.05	1.87	1.20	0.67	0.47	0.39	0.30	..
Anthracene	68	9.38	8.40	7.81	6.80	5.97	5.29	4.80	4.42
2-Naphthol	68	9.29	8.27	7.88	6.50	5.79	5.39	4.90	4.60

at temperatures other than 74°. In one case, however, 2,4,6-trinitrostilbene at a concentration of 2 moles per 100 moles of TNT (2.7 weight %) reduced the LCV at 63.8° to less than 5% of the normal rate, while the most effective additive described by Pelchowicz and Bergmann, 2,4,6-trinitrophenylethyl benzoate at the 3% level (by weight) reduced the rate to only 10% of normal at 60°. However, preliminary information indicates the existence of anomalies in the LCV of certain TNT systems at lower temperatures which preclude extrapolation. These anomalies will be the subject of a subsequent communication.

In considering the effect of the nature of the groups attached to the trinitrophenyl group, examination of the LCV data yields the following generalizations.

1. Derivatives of trinitrobenzene with a phenyl or substituted phenyl group attached through some linkage are the most crystal-growth active.

2. An ethylenic bridge, as in the stilbenes, creates greater activity in the molecule than do the linkages

$$-O-, \quad -\underset{H}{\underset{|}{N}}-\underset{H}{\underset{|}{N}}-, \quad -N=N-, \quad -S-, \quad -O-C_2H_4-O-,$$

and
$$-O-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O-$$

3. Where the attached phenyl group is substituted, greater activity is observed, with substitution in the 3'- or 4'-positions causing about equal increases in crystal growth activity, with substitution in the 2'-position causing considerably more activity.

4. Increasing the molecular weight of the additive decreases the activity; 1,3-bis-(2,4,6-trinitrophenyl)-2-phenylpropane and p-di-(2,4,6-trinitrophenylethenyl)-benzene are less effective on a weight basis than 2,4,6-trinitrostilbene.

Two exceptions to the general statement of superior effectiveness of compounds containing the trinitrophenyl group were found. The LCV data indicate that both benzaldehyde 2,4-dinitrophenylhydrazone and 2,2',4,4'-tetranitrostilbene exhibit a high order of growth activity.

Mechanism of Retardation.—In considering the means by which small amounts of foreign molecules can effect remarkable reductions in the linear crystallization velocity, the concept of adsorption appears most useful. It was determined that the

viscosities of TNT melts were not appreciably altered by the addition of 2% of several additives, yet in the case of 2,4,6-trinitrostilbene this concentration was able to reduce the crystallization rate to approximately 10% of that of pure TNT. Further it has been shown by Campbell and Pritchard[24] that the addition of 1% nitrocellulose to a mixture of 55% picric acid–45% dinitrophenol caused an eight time increase in viscosity and yet increased the linear crystallization velocity 1.2 times. Likewise the surface tension of TNT was little affected by the inclusion of similar quantities of several additives including 2,4,6-trinitrostilbene. Further it was not possible to demonstrate any correlation between the eutectic temperature or the eutectic composition and the effect of the second component on the crystallization velocity of TNT.

The long recognized and more thoroughly studied phenomenon[26] of modification of crystal habit effected by crystallization from solutions containing adsorbable impurities lends credence to the belief that a similar mechanism is operative in crystallization from a melt. In an attempt to obtain corroboration for this mechanism, the adsorption behavior of a series of polynitrostilbenes was studied by chromatographic techniques.[27] On silicic acid–Celite, the relative adsorption affinities were found to correspond quite closely to effectiveness in reducing the LCV of TNT. On Kaolin–Celite, however, the relative affinities were almost completely reversed. Such anomalous results, while incapable of adequate explanation, do not argue against the adsorption concept, since it must be accepted that adsorption processes depend upon the system in its entirety.

The fact that in general the most effective additives contain the trinitrophenyl group in the molecule allows the postulate that this part of the molecule with its structural similarity to TNT could attach to the growing crystal face in the place of a TNT molecule. Since these foreign molecules contain a bulky group attached to the trinitrophenyl group, however, this tail could prevent the attachment of TNT molecules in some area immediately adjacent. This affected area would depend somewhat on the size of the tail

(26) W. A. France, "Adsorption and Crystal Habit Modification" in J. Alexander, "Colloid Chemistry," Vol. V, Reinhold Publ. Corp., New York, N. Y., 1945, pp. 443–57; H. E. Buckley, "Crystal Growth," John Wiley and Sons, Inc., New York, N. Y., 1951, Chap. 10; "Crystal Growth," Far. Soc. Discussions, No. 5, 1949.

(27) A. F. Teague, W. A. Gey and R. W. Van Dolah, Anal. Chem., 27, 785 (1955).

and its steric relationship to the substrate surface. There is some permanent adsorption of the additive, since LCV determinations on material fractionated by a partial freezing technique show little, if any, change in the concentration of the additive. This allows another possible modification of the physical concept of growth inhibition. It may well be that the additives are "adsorbed" not in the form of single molecules but rather as conglomerates or crystallites. Such adsorption or attachment to the substrate surface could be possible if the crystals of additive were isomorphous with TNT or if a face of the additive crystallite were compatible with a face of the substrate. The absence of adequate crystallographic data on the compounds studied precludes a determination of isomorphism.

The absence of any change in additive concentration is not too surprising, since the effects observed here are quite different from the usual case of adsorption on charcoal. In these latter cases there is an opportunity for equilibrium to be attained throughout the system because of mixing. With a relatively slow-growing crystal front, equilibrium can only be expected in a very narrow discrete volume around the crystals, and with the slow diffusion of the large additive molecules one can expect eutectic crystallization more or less throughout the mass, if the temperature is below the eutectic temperature. Whether the concept of molecular attachment or crystallite attachment is used, it is to be expected that this is a reversible process and that the additive particles may be displaced.

This explanation of crystal-growth activity fits well with a recent proposal on the method of crystal growth,[28] which postulates a spiraling addition of molecules or groups of molecules, starting at a dislocation. If an effective additive is present, very small amounts can exhibit a tremendous effect on the rate of growth during the period of its attachment.

Adsorption Isotherms.—Considering this mechanism an effort was made to evaluate the LCV *versus* additive concentration data by means of the Freundlich isotherm. Figure 4 illustrates the rather poor fit of the data in this relationship. While
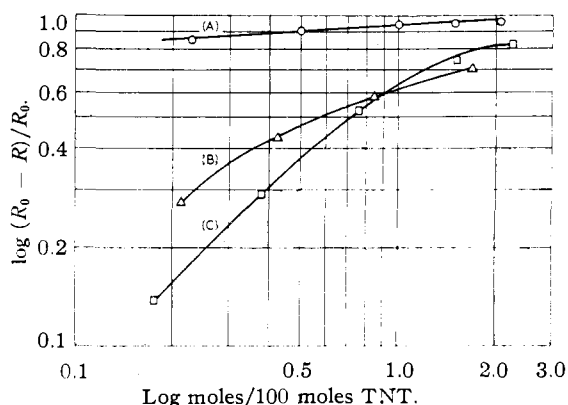
Fig. 4.—Freundlich isotherm of TNT plus additives at 74.0°: (A) 2'-chloro-2,4,6-trinitrostilbene; (B) 2,4-dinitrostilbene; (C) 2,4,6-trinitrodiphenyl ether.

(28) F. C. Frank, *Faraday Soc. Disc.*, **5**, 48 (1949).

Freundlich stated that the values of $1/n$ should be 0.2 to 0.7, the values for some of the more effective additives to TNT were found to be less than 0.1.

In order to obtain an equation giving better fit to the data, one based on the Langmuir theory of reversible adsorption was developed. The terms were defined as:

C　　 = mole fraction of substrate (TNT)
$1 - C$ = mole fraction of additive
θ　 = fraction of crystal surface covered by the additive
R_0　 = LCV of the pure substrate
R　 = LCV of the substrate plus additive

Then the rate of growth of the solid may be expressed as

$$R = R_0 C(1 - \theta) \tag{1}$$

The rate of adsorption of the additive is

$$r_a = K_1(1 - C)(1 - \theta) \tag{2}$$

and the rate of desorption is

$$r_d = K_2 \theta \tag{3}$$

At equilibrium, eq. 2 and 3 may be equated and solved for $(1 - \theta)$, which is substituted in eq. 1 to yield

$$R = \frac{R_0 C}{1 + \alpha(1 - C)} \tag{4}$$

where $\alpha = K_1/K_2$.

Figures 5 and 6 show plots of the data for poorly adsorbed additives and for strongly adsorbed additives, respectively. In the first instance, although the data are limited, there is agreement at low concentrations; but at concentrations of additive above about one mole per cent. there is considerable deviation from linearity, indicating that the equation offers an incorrect picture of the phenomena at higher concentrations. In Fig. 6 straight lines are obtained, but all have intercepts other than 1. This can be interpreted as due to the additives being more than normally effective at low concentrations, which could be caused by irreversible adsorption. As the first approximation, eq. 4 was modified by the empirical addition of a second constant, β, to yield

$$R = \frac{R_0 C}{1 + \beta + \alpha(1 - C)} \tag{5}$$

Such an equation describes the data adequately over a considerable range of concentrations; the calculated constants for some additives are listed in Table VII.

The values of α and β bear an apparent relationship to R_0 since they are derived from data obtained for regions of reasonable concentrations of additive and it has been shown that with such concentrations the LCV is insensitive to the R_0 of the starting material (TNT). This is interpreted, following the adsorption hypothesis, as resulting from the competition for adsorption sites, and thus for the role of rate inhibitor, between the adventitious impurities and the deliberate additive. In the absence of very effective additives, the impurities exert an effect on crystallization but as the concentration of the more effective materials becomes appreciable the impurities are displaced and their effect becomes steadily smaller.

An examination of this equation in the light of the LCV data for TNT shows that for non-adsorp-

Table VII

Values of Constants in Equation 5 for Additives to TNT

Compound	Temp., °C.	Constant α	β
2,4-Dinitrotoluene	74	23.0	0.00
2,4,4'-Dinitrostilbene	74	180	0.15
Benzaldehyde 2,4-dinitrophenyl-	67.6	253	0.80
hydrazone	74	498	0.70
4'-Phenyl-2,4,6-trinitrostilbene	74	524	0.00
2,4,6-Trinitrostilbene	74	615	1.35
	68	1590	0.90
	63.8	820	1.35
4'-Hydroxy-2,4,6-trinitrostilbene	74	640	2.90
4'-Methoxy-2,4,6-trinitrostilbene	74	724	2.20
3'-Nitro-2,4,6-trinitrostilbene	74	778	3.00
4'-Nitro-2,4,6-trinitrostilbene	74	786	2.25
2'-Methoxy-2,4,6-trinitrostilbene	74	832	1.80
3'-Iodo-2,4,6-trinitrostilbene	74	1057	2.60
2'-Chloro-2,4,6-trinitrostilbene	74	1788	2.50

tion, or mere dilution, α and β should become equal to 0, and the equation reduces to

$$R = R_0C \qquad (6)$$

Thus a plot of R (or LCV) against C should yield a straight line with a slope equal to R_0. While, as can be seen in curve A, Fig. 2, dinitropropane does follow a straight line, the slope is much greater than R_0. This is taken as indicating that in all the cases studied there is always some adsorption of the foreign molecules. The failure of poorly adsorbed additives to conform to eq. 5 may be due to the combination of dilution and adsorption characteristics.

The derivation of eq. 5, as described, fails to provide for either the extreme rate-affecting characteristics of certain efficient additives at low concentrations or an adequate physical basis for the addition of the empirical constant β. If R_0C/R is plotted against the concentration of additive $(1 - C)$ it may be observed that low concentrations of additives are more efficient inhibitors than high concentrations. That is, the first 0.1% reduces the rate more than does 1.1% over 1.0%. Above a small, critical concentration the effectiveness per increment of additive levels off to a constant value. An explanation for this phenomenon is offered on the basis of the following physical model and derivation.

Considering the mechanism of crystal growth to follow the spiral dislocation theory, retardation of growth may be accomplished by adsorption of additive molecules at critical sites. It is assumed that a single additive molecule occupying such a critical site may inhibit the growth of a considerable surrounding area of substrate.[29] The additives may desorb which then allows growth from that site, effecting however an over-all retardation of crystallization; or it may be fixed in place by overgrowth by the substrate which may be likened to solid solution formation, or by the self-adsorption of a second (or more) additive molecule. In this latter case, which may be seen to approach eutectic

(29) A similar concept applied to crystallization from solution has been discussed by A. F. Wells in "Structure and Properties of Solid Surfaces," R. Gomer and C. S. Smith, eds., University of Chicago Press, Chicago, Ill., 1953, pp. 244–245.
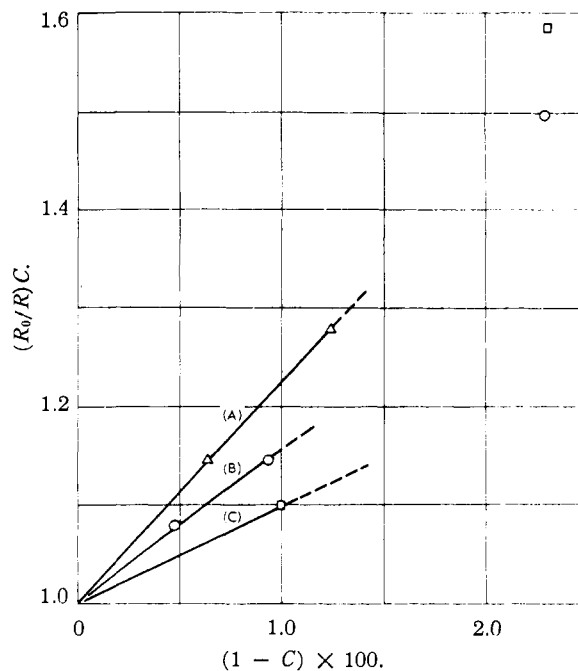

Fig. 5.—Langmuir isotherm of TNT plus poorly adsorbed additives at 74.0°: (A) 2,4-dinitrotoluene; (B) 2,2-dinitropropane; (C) β-phenoxy-ethanol. (α = 23.0, 15.7 and 10.0, respectively.)
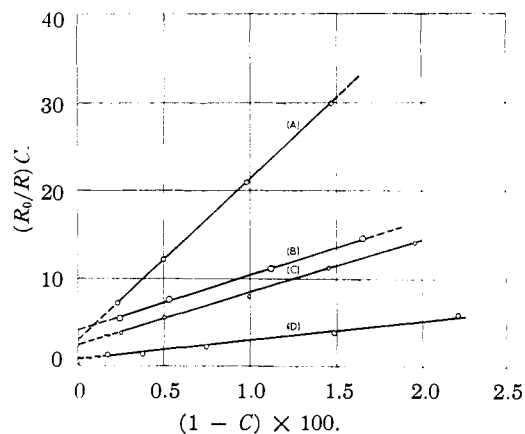

Fig. 6.—Langmuir isotherm of TNT plus strongly adsorbed additives at 74.0°: (A) 2'-chloro-2,4,6-trinitrostilbene; (B) 4'-hydroxy-2,4,6-trinitrostilbene; (C) 2,4,6-trinitrostilbene; (D) 2,4,6-trinitrodiphenyl ether.

crystallization, one molecule or several molecules of additive depositing on an adsorbed additive molecule only suffice to fix that molecule in place and do not contribute significantly to the covering of the substrate surface affected.

Now if, as before, θ is taken as the fraction of surface (or growth sites) occupied by additive molecules and $(1 - \theta)$ the fraction of surface available for growth of the substrate or for adsorption of the additive and $(1 - C)$ as the concentration of the additive, the expressions used above for rate of crystallization (eq. 1) and rate of adsorption (eq. 2) may be retained. The expression for the rate of desorption, however, must reflect the conversion of adsorbed additive molecules from a desorbable

state to a non-desorbable state. Such an expression is

$$r_d = K_2\theta - K_3(1 - \theta)\lambda \tag{7}$$

in which the second term reflects the rate of conversion to a non-desorbable state. This latter rate is taken as being proportional to $(1 - \theta)$, the fraction of the free surface (number of unoccupied growth sites) which is a measure of the tendency for overgrowth by the substrate, and to λ, the fraction of occupied growth sites (θ) which have multiple occupancy. The term λ may be seen to vary with concentration as

$$\Delta\lambda \alpha \Delta(1 - C)(1 - \lambda) \tag{8}$$

Thus the probability of an additive molecule adsorbing on another already on the surface and thus rendering the first non-desorbable, is proportional to the additive concentration in the melt and to the concentration of singly adsorbed molecules in the adsorbed surface $(1 - \lambda)$ since the adsorption of more additive molecules on the first only fixes one on a critical site.

Written in differential form

$$\frac{d\lambda}{1 - \lambda} = K_4 d(1 - C) \tag{9}$$

and integrating one obtains

$$\lambda = 1 - e^{-K_4(1-C)} + A \tag{10}$$

at $(1 - C) = 0, \lambda = 0$, thus $A = 0$.

Substitution in equation 7 and equating with equation 2 yields

$$K_1(1 - C)(1 - \theta) = K_2\theta - K_3(1 - \theta)(1 - e^{-K_4(1-C)}) \tag{11}$$

from which one obtains

$$(1 - \theta) = \frac{1}{1 + \alpha(1 - C) + \beta(1 - e^{-K_4(1-C)})} \tag{12}$$

where

$$\alpha = \frac{K_1}{K_2} \text{ and } \beta = \frac{K_3}{K_2}$$

Substitution in (1) gives

$$\frac{R_0C}{R} = 1 + \alpha(1 - C) + \beta(1 - e^{-K_4(1-C)}) \tag{13}$$

To evaluate the α and β, R_0C is plotted *versus* $(1 - C)$. The slope of the linear portion of the curve is α. The extrapolated intercept of this same portion is $\beta + 1$ since at large values of $(1 - C)$, the exponential term approaches zero. Differentiating

the expression with respect to $(1 - C)$ gives

$$d\left(\frac{R_0C}{R}\right) / d(1 - C) = \alpha + K_4\beta e^{-K_4(1-C)} \tag{14}$$

Thus as $1 - C$ approaches zero it reduces to $\alpha + K_4\beta$ which is then the initial slope of the curve. The constants for this equation for use at 74° with $R_0 = 2.50$ have been evaluated in a limited number of instances and are given below

Compound	α	β	K
p-Di-(β-2,4,6-trinitrophenylethenyl)-benzene	934	0.30	26537
2,4,6-Trinitrostilbene	615	1.35	2452
3'-Iodo-2,4,6-trinitrostilbene	1057	2.60	2252

Considering equation 14 it may be seen that at very low concentrations there is a considerable contribution to the retardation (R_0C/R) by the permanent occupancy of growth sites by additive molecules. As the concentration increases, however, there are three competing factors. The tendency for overgrowth will be reduced by more growth sites being occupied by additives but the tendency for multiple adsorption at a single site will be increased. However, this latter reduces the efficiency of the additive since, as pointed out above, one or several clumped molecules only prevent growth from one site. These competing factors tend to approach a balance at high concentrations and the equation reduces to the original form relating retardation to concentration by a constant of proportionality which is the ratio of the rate constants for the reversible adsorption and desorption processes. The constant β similarly represents a ratio of rate constants for the conversion to permanent occupancy and reversible adsorption or, in other words, the ratio of rate constants for irreversible adsorption to reversible adsorption.

Thus there is now developed an expression which describes the growth retarding effects of strongly adsorbed additives over the complete range of concentration studies, accounting for the extraordinary effectiveness of very low concentrations.

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