Table V. Pore Volume of Inorganic Particles

	Pore Volume					
Source of Inorganic Particles[a]	$P/P_0 = 0.96$		$P/P_0 = 0.90$		Intraparticle O.M.,[d] Vol. %	
	Ml./g.	Porosity, %	Ml./g.	Porosity, %	$P/P_0 = 0.96$	$P/P_0 = 0.90$
28.6[b]	0.0096	2.66	0.0050	1.39	6.36	3.31
75[b]	0.0086	2.36	0.0029	0.80	2.06	0.70
75[c]	0.0079	2.16	0.0048	1.31	...	...

[a] Gal. per ton of shale. [b] Initial inorganic particles. [c] Free of water-soluble material. [d] Organic matter.

Table VI. Estimated Amount of Organic Matter in Contact with the Mineral Constituents

Source of Mineral Constituents	Surface Area, Sq. M./G.	Diam. of Organic Molecule, A.	O.M.[a] Per Monolayer, Wt. %	Total O.M.,[a] No. of Monolayers
28.6 Gal./Ton Shale	4.24	20	3.11	32
	4.24	10	1.57	64
75 Gal./Ton Shale	3.12	20	0.57	175
	3.12	10	0.29	345

[a] O.M. = organic matter.

structure and that the distribution of the organic matter within the two shales is essentially inter- rather than intraparticle. Therefore, only a small part of the organic matter has to diffuse through the inorganic particles' micropore structure when it is removed from the shale.

Organic Matter in Contact with the Mineral Constituents. Using surface area data and the following assumptions, an estimate was made of the amount of organic matter in contact with the mineral constituents. The assumptions were: The organic molecules were spheres, 10 or 20 A. in diameter; the total surface of the mineral constituents was available for contact; and that the spherical molecules formed a rectangular pattern on the surface. Based on the density of the organic matter, the respective molecular weights of these molecules would be about 340 and 2700. Table VI presents the amount of organic matter represented by one monomolecular layer in contact with the surface, and it also presents the number of monolayers the total organic matter could form if evenly distributed over the surface of the mineral constituents. These estimates suggest that only a small part of the organic matter is bonded either physically or chemically to the mineral constituents.

LITERATURE CITED

(1) Barr, W.E., Anhorn, V.J., "Scientific and Industrial Glass Blowing and Laboratory Techniques," p. 257, Instruments Publishing Co., Pittsburgh, Pa., 1949.

(2) Brunauer, S., "The Adsorption of Gases and Vapors," p. 95, Princeton University Press, Princeton, N.J., 1943.

(3) Brunauer, S., Emmett, P.H., Teller, E.J., *J. Am. Chem. Soc.* **60**, 309 (1938).

(4) Emmett, P.H., "Catalysis," Vol. **1**, p. 31, Reinhold, New York, 1954.

(5) Emmett, P.H., *Ind. Eng. Chem.* **37**, 639 (1945).

(6) Emmett, P.H., Brunauer, S., *J. Am. Chem. Soc.* **59**, 1553 (1937).

(7) Reis, H.E., Jr., "Advances in Catalysis," Vol. **4**, p. 87, Academic Press, New York, 1952.

(8) Stanfield, K.E., Frost, I.C., McAuley, W.S., Smith, H.N., U. S. Bur. of Mines Rept. Invest. 4825, p. 18, November 1951.

(9) Tisot, P.R., Murphy, W.I.R., J. CHEM. ENG. DATA **5**, 558 (1960).

RECEIVED for review December 20, 1961. Accepted April 6, 1962. Division of Fuel Chemistry, 140th Meeting, ACS, Chicago, Ill., September, 1961. Work done under a cooperative agreement between Bureau of Mines, U. S. Department of the Interior and University of Wyoming.

Polynitro Carbamates and *N*-Nitrocarbamates

MILTON B. FRANKEL[1]
Chemical Division of Aerojet-General Corp., Azusa, Calif.

IN RECENT YEARS there has been a great deal of interest in high energy compounds for use in explosive and propellant compositions. Polynitro aliphatic compounds constitute a new class of high energy materials and the present work describes the synthesis of several classes of these substances. The preparation of polynitro carbamates and *N*-nitrocarbamates is described in this paper while the synthesis of polynitro aliphatic nitramines is presented in a following article.

Carbamates are conveniently prepared by the addition of an alcohol to an isocyanate. Utilization of nitro alcohols and nitro isocyanates leads to the formation of polynitro carbamates. The nitro alcohols, such as 2,2,2-trinitroethanol, were prepared by the condensation of the corresponding nitro alkanes and formaldehyde (2). The nitro isocyanates were synthesized by the Curtius degradation of the corresponding acid chlorides (*4*).

Nitro alcohols are more acidic and react less readily with isocyanates than ordinary alcohols. However, when the reaction is catalyzed with a trace of ferric acetylacetonate (5), addition occurs readily. Thus, on refluxing the reactants in chloroform for 6 to 8 hours, in most cases quantitative yields of the addition products were obtained. In those cases in which the carbamate was an oil, no attempt was made at purification through distillation because of the high oxygen content. The crude oils were nitrated directly, following the procedure of Curry and Mason (*1*), to give solid products which could be easily purified. Twenty-two new carbamates (Table I) and 25 new *N*-nitrocarbamates (Table II) were prepared. Many of these

---

[1] Present address, Stanford Research Institute, Menlo Park, Calif.

Table I. Properties of Carbamates

Isocyanate	Alcohol	Carbamate	Yield, %	Uncorrected M.P., ° C.	Recrystallization Solvent	Formula	Analyses Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
CH_3NCO	$(NO_2)_3CCH_2OH$	$CH_3NHCO_2CH_2C(NO_2)_3$	Quant.	oil		$C_4H_6N_4O_8$						
C_2H_5NCO	$(NO_2)_3CCH_2OH$	$C_2H_5NHCO_2CH_2C(NO_2)_3$	Quant.	oil		$C_5H_8N_4O_8$						
$C_2H_5O_2CCH_2NCO$	$(NO_2)_3CCH_2OH$	$C_2H_5O_2CCH_2NHCO_2CH_2C(NO_2)_3$	Quant.	71–72	Carbon tetrachloride	$C_7H_{10}N_4O_{10}$	27.10	3.25	18.06	27.47	3.45	17.90
$CH_3N(NO_2)CH_2CH_2NCO$	$(NO_2)_3CCH_2OH$	$CH_3N(NO_2)CH_2CH_2NHCO_2CH_2C(NO_2)_3$	Quant.	98–99	Chloroform	$C_6H_{10}N_6O_{10}$	22.09	3.09		22.06	3.06	
$CH_3C(NO_2)_2CH_2CH_2NCO$	$CH_3C(NO_2)_2CH_2OH$	$CH_3C(NO_2)_2CH_2CH_2NHCO_2CH_2C(NO_2)_2CH_3$	Quant.	oil		$C_8H_{13}N_5O_{10}$						
$CH_3C(NO_2)_2CH_2CH_2NCO$	$(NO_2)_3CCH_2OH$	$CH_3C(NO_2)_2CH_2CH_2NHCO_2CH_2C(NO_2)_3$	Quant.	oil		$C_7H_{10}N_6O_{12}$						
$CH_3C(NO_2)_2CH_2N(NO_2)CH_2NCO$	$(NO_2)_3CCH_2OH$	$CH_3C(NO_2)_2CH_2N(NO_2)CH_2NHCO_2CH_2C(NO_2)_3$	Quant.	oil		$C_7H_{10}N_8O_{14}$						
$(NO_2)_3CCH_2CH_2NCO$	C_2H_5OH	$(NO_2)_3CCH_2CH_2NHCO_2C_2H_5$	49.2	65–66	Cyclohexane	$C_6H_{10}N_4O_8$	27.07	3.79	21.05	27.63	3.94	21.56
$(NO_2)_3CCH_2CH_2NCO$	$C_6H_{11}OH$	$(NO_2)_3CCH_2CH_2NHCO_2C_6H_{11}$	40.6	96–97	Cyclohexane	$C_{10}H_{16}N_4O_8$	37.52	5.04	17.51	37.59	5.00	17.09
$(NO_2)_3CCH_2CH_2NCO$	C_6H_5OH	$(NO_2)_3CCH_2CH_2NHCO_2C_6H_5$	63.7	102–103	Ethanol-water	$C_{10}H_{10}N_4O_8$	38.22	3.21	17.83	38.46	3.23	17.63
$(NO_2)_3CCH_2CH_2NCO$	$CH_3C(NO_2)_2CH_2OH$	$(NO_2)_3CCH_2CH_2NHCO_2CH_2C(NO_2)_2CH_3$	91.7	103–104	Chloroform	$C_7H_{10}N_6O_{12}$	23.34	2.80	23.33	22.98	2.80	22.90
$(NO_2)_3CCH_2CH_2NCO$	$(NO_2)_3CCH_2OH$	$(NO_2)_3CCH_2CH_2NHCO_2CH_2C(NO_2)_3$	81.7	91–92	Carbon tetrachloride	$C_6H_7N_7O_{14}$	17.96	1.76	24.44	18.36	1.82	23.77
$CH_3C(NO_2)_2CH_2CH_2NCO$	$C(NO_2)_2\text{-}[CH_2OH]_2$	$[CH_3C(NO_2)_2CH_2CH_2NHCO_2CH_2]_2\text{-}C(NO_2)_2$	Quant.	128–129	Chloroform	$C_{13}H_{20}N_8O_{16}$	28.68	3.70	20.59	29.13	3.91	20.82
$(NO_2)_3CCH_2CH_2NCO$	$C(NO_2)_2\text{-}[CH_2OH]_2$	$[(NO_2)_3CCH_2CH_2NHCO_2CH_2]_2\text{-}C(NO_2)_2$	Quant.	oil		$C_{11}H_{14}N_{10}O_{20}$						
$(NO_2)_3CCH_2CH_2NCO$	$HOCH_2C\equiv CCH_2OH$	$[(NO_2)_3CCH_2CH_2NHCO_2CH_2C]_2\equiv$	Quant.	oil		$C_{12}H_{14}N_8O_{16}$						
$CH_2[NCO]_2$	$(NO_2)_3CCH_2OH$	$CH_2[NHCO_2CH_2C(NO_2)_3]_2$	46.6	125–126	Chloroform	$C_7H_8N_8O_{16}$	18.27	1.75	24.35	18.40	1.64	23.73
$C(NO_2)_2\text{-}[CH_2CH_2NCO]_2$	$(NO_2)_3CCH_2OH$	$C(NO_2)_2\text{-}[CH_2CH_2NHCO_2CH_2C(NO_2)_3]_2$	61.8	96–97	Chloroform	$C_{11}H_{14}N_{10}O_{20}$	21.79	2.33	23.10	22.37	2.42	23.71
$N(NO_2)\text{-}[CH_2NCO]_2$	$(NO_2)_3CCH_2OH$	$N(NO_2)\text{-}[CH_2NHCO_2CH_2C(NO_2)_3]_2$	Quant.	oil		$C_8H_{10}N_{10}O_{18}$						
$OCNCH_2N(NO_2)CH_2CH_2NCO$	$(NO_2)_3CCH_2OH$	$(NO_2)_3CCH_2O_2CNHCH_2N(NO_2)CH_2CH_2NHCO_2CH_2C(NO_2)_3$	86.7	65–67	Ethylene dichloride	$C_9H_{12}N_{10}O_{18}$	19.71	2.21	25.55	20.29	2.45	25.21
$N(NO_2)\text{-}[CH_2NCO]_2$	$(NO_2)_3CCH_2OH$	$N(NO_2)\text{-}[CH_2CH_2NHCO_2CH_2C(NO_2)_3]_2$	92.5	130–131	Ethylene dichloride	$C_{10}H_{14}N_{10}O_{18}$	21.36	2.51	24.91	21.87	2.70	25.38
$[CH_2N(NO_2)CH_2CH_2NCO]_2$	$(NO_2)_3CCH_2OH$	$[CH_2N(NO_2)CH_2CH_2NHCO_2CH_2C(NO_2)_3]_2$	85.7	156–158	Ethylene dichloride	$C_{12}H_{18}N_{12}O_{20}$						
$N(NO_2)\text{-}[CH_2C(NO_2)_2CH_2CH_2NCO]_2$	$(NO_2)_3CCH_2OH$	$N(NO_2)\text{-}[CH_2C(NO_2)_2CH_2CH_2NHCO_2CH_2C(NO_2)_3]_2$	91.3	157–159	Methanol-water	$C_{14}H_{18}N_{14}O_{26}$	21.06	2.27	24.56	21.34	2.59	25.37

Table II. Properties of *N*-Nitrocarbamates

N-Nitrocarbamate	Yield, %	M.P., ° C.	Recrystallization Solvent	Formula	Analyses Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
$CH_3N(NO_2)CO_2CH_2C(NO_2)_3$	74.3	39–40	Diisopropyl ether	$C_4H_5N_5O_{10}$	16.97	1.78	24.74	17.29	1.86	24.91
$C_2H_5N(NO_2)CO_2CH_2C(NO_2)_3$	85.7	50–51	Carbon tetrachloride	$C_5H_7N_5O_{10}$	20.21	2.38	23.57	20.55	2.04	23.68
$C_2H_5O_2CCH_2N(NO_2)CO_2CH_2C(NO_2)_3$	81.2	46–47	Isopropyl alcohol-water	$C_7H_9N_5O_{12}$	23.67	2.55	19.72	23.98	2.95	20.18
$CH_3N(NO_2)CH_2CH_2N(NO_2)CO_2CH_3$	95.8	57–58	Methanol	$C_5H_{10}N_4O_6$	27.03	4.54	25.22	27.19	4.49	25.55
$CH_3N(NO_2)CH_2CH_2N(NO_2)CO_2CH_2C(NO_2)_3$	87.2	103–104	Chloroform	$C_6H_8N_7O_{12}$	19.41	2.44	26.42	19.68	2.37	25.92
$CH_3C(NO_2)_2CH_2CH_2N(NO_2)CO_2CH_2C(NO_2)_2CH_3$	92.8	70–72	Chloroform	$C_8H_{12}N_6O_{12}$	25.01	3.15	21.88	25.96	3.66	21.73
$CH_3C(NO_2)_2CH_2CH_2N(NO_2)CO_2CH_2C(NO_2)_3$	40.5	107–108	Chloroform	$C_7H_9N_7O_{14}$	20.25	2.19	23.62	20.26	2.21	23.67
$CH_3C(NO_2)_2CH_2N(NO_2)CH_2N(NO_2)CO_2CH_3$	90.2	105–106	Isopropyl alcohol	$C_6H_{10}N_6O_{10}$	22.09	3.09	25.77	22.50	3.03	25.70
$CH_3C(NO_2)_2CH_2N(NO_2)CH_2N(NO_2)CO_2CH_2C(NO_2)_3$	63.5	140–141	Ethylene dichloride	$C_7H_9N_9O_{16}$	17.69	1.91	26.53	18.08	1.95	26.58
$(NO_2)_3CCH_2CH_2N(NO_2)CO_2C_2H_5$	70.0	94–95	Carbon tetrachloride	$C_9H_8N_5O_{10}$	23.16	2.92	22.51	23.44	2.97	23.14
$(NO_2)_3CCH_2CH_2N(NO_2)CO_2C_6H_{11}$	95.0	56–58	Ethanol-water	$C_{10}H_{15}N_5O_{10}$	32.88	4.14	19.18	33.25	4.21	18.82
$(NO_2)_3CCH_2CH_2N(NO_2)CO_2C_6H_4NO_2$	38.4	127–129	Carbon tetrachloride	$C_{10}H_8N_6O_{12}$	29.71	2.00	20.79	29.22	2.04	19.73
$(NO_2)_3CCH_2CH_2N(NO_2)CO_2CH_2C(NO_2)_2CH_3$	83.7	71–72	Chloroform	$C_7H_9N_7O_{14}$	20.25	2.19	23.62	20.51	2.22	24.05
$(NO_2)_3CCH_2CH_2N(NO_2)CO_2CH_2C(NO_2)_3$	89.4	96–97	Carbon tetrachloride	$C_0H_8N_6O_{16}$	16.15	1.36	25.12	16.35	1.36	25.34
$[CH_3C(NO_2)_2CH_2CH_2N(NO_2)CO_2CH_2]_2\text{-}C(NO_2)_2$	88.0	117–118	Ethylene dichloride	$C_{13}H_{18}N_{10}O_{20}$	24.61	2.86	22.08	24.78	2.90	21.87
$[(NO_2)_3CCH_2CH_2N(NO_2)CO_2CH_2]_2\text{-}C(NO_2)_2$	89.7	94–96	Chloroform	$C_{11}H_{12}N_{12}O_{24}$	18.97	1.74	24.14	19.29	2.00	24.21
$[(NO_2)_3CCH_2CH_2N(NO_2)CO_2CH_2C]_2\equiv$	60.0	115–116	Chloroform	$C_{12}H_{12}N_{10}O_{20}$	23.38	1.96	22.73	23.61	2.19	22.60
$(NO_2)_3CCH_2O_2CNHCH_2N(NO_2)CO_2CH_2C(NO_2)_3$	90.0	103–104	Chloroform	$C_7H_7N_9O_{18}$	16.64	1.40	24.96	16.66	1.25	24.44
$(NO_2)_3CCH_2O_2CN(NO_2)CH_2N(NO_2)CO_2CH_2C(NO_2)_3$	95.0	95–96[a] 112–113[a]	Chloroform	$C_7H_0N_{10}O_{20}$	15.28	1.10	25.46	15.53	1.26	24.96
$C(NO_2)_2\text{-}[CH_2CH_2N(NO_2)CO_2CH_2C(NO_2)_3]_2$	85.8	151–152	Methylene chloride	$C_{11}H_{12}N_{12}O_{24}$	18.97	1.74	24.14	19.19	1.77	23.87
$N(NO_2)\text{-}[CH_2N(NO_2)CO_2CH_2C(NO_2)_3]_2$	62.3	185–186	Ethylene dichloride	$C_8H_8N_{12}O_{22}$	15.39	1.39	26.93	15.71	1.31	26.35
$(NO_2)_3CCH_2O_2CN(NO_2)CH_2N(NO_2)CH_2CH_2N(NO_2)CO_2CH_2C(NO_2)_3$	62.8	113–114	Ethylene dichloride	$C_9H_{10}N_{12}O_{22}$	16.94	1.58	26.34	16.98	1.59	25.61
$N(NO_2)\text{-}[CH_2CH_2N(NO_2)CO_2CH_2C(NO_2)_3]_2$	86.3	120–122	Ethylene dichloride	$C_{10}H_{12}N_{12}O_{22}$	18.41	1.86	25.77	18.98	2.23	25.87
$[CH_2N(NO_2)CH_2CH_2N(NO_2)CO_2CH_2C(NO_2)_3]_2$	87.8	127–128	70% Nitric acid	$C_{12}H_{16}N_{14}O_{24}$	19.47	2.18	26.49	19.51	2.29	25.78
$N(NO_2)\text{-}[CH_2C(NO_2)_2CH_2CH_2N(NO_2)CO_2CH_2C(NO_2)_3]_2$	93.3	150–151	Ethylene dichloride	$C_{14}H_{18}N_{16}N_{16}O_{30}$	18.93	1.82	25.23	19.12	1.84	25.19

[a] Polymorphic forms, nitration carried out at 45°.

compounds were disclosed in a series of patents (*3*). The *N*-nitrocarbamates are white crystalline solids with excellent thermal stability, they are generally sensitive to impact and should be handled with care.

EXPERIMENTAL

Preparation of Carbamate. The preparation of *N*-(3,3,3-trinitopropyl)-2,2,2-trinitroethyl carbamate is given as typical. A mixture of 42.2 grams (0.19 mole) of 3,3,3-trinitropropyl isocyanate, 34.7 grams (0.19 mole) of 2,2,2-trinitroethanol, 300 ml. of dry, alcohol free chloroform, and a trace of ferric acetylacetonate was placed in a 1-liter round-bottomed flask, fitted with a condenser and drying tube. The solution was refluxed for 8 hours and concentrated in vacuo to give 62.8 grams (81.7%) of a white solid, m.p. 77 to 86° C. Recrystallization from carbon tetrachloride gave a melting point of 91 to 92° C.

Preparation of N-Nitrocarbamate. The preparation of *N*-nitro-*N*-(3,3,3-trinitropropyl)-2,2,2-trinitroethyl carbamate is given as typical. A quantity of 250 ml. of absolute nitric acid (Technical Grade) was cooled in an ice-salt bath, and 250 ml. of acetic anhydride was added dropwise with stirring, while the temperature was kept below 10° C. Then 68.6 grams (0.17 mole) of *N*-(3,3,3-trinitropropyl)-2,2,2-trinitroethyl carbamate was added portionwise at 5° C., and stirring was continued for an additional 30 minutes. The solution was poured with stirring onto cracked ice, the white solid was collected, washed well with cold water, and dried in vacuo over potassium hydroxide to give 68.1 grams (89.4%) of product, m.p. 83 to 90° C. Recrystallization from carbon tetrachloride raised the melting pount to 96 to 97° C.

In those cases in which the carbamate was an oil, the oil was dissolved in the acetic anhydride, and the solution was added dropwise to the absolute nitric acid at 5 to 10° C.

ACKNOWLEDGMENT

The author is indebted to the Office of Naval Research for the financial support of this work. Microanalyses were performed by A. Elek, Elek Microanalytical Laboratories, Los Angeles, Calif.

LITERATURE CITED

(1) Curry, H.M., Mason, J.P., *J. Am. Chem. Soc.* **73**, 5043 (1951).
(2) Feuer, H., Kucera, T.J., *J. Org. Chem.*, **25**, 2069 (1960).
(3) Frankel, M.B., U. S. Patents **2,978,485** through **2,978,493**, April 4, 1961.
(4) Gold, M.H., Frankel, M.B., Linden, G.B., Klager, K., *J. Org. Chem.*, **27**, 334 (1962).
(5) Peterson, S., *Ann.* **562**, 206 (1949).

RECEIVED for review October 30, 1961. Accepted January 8, 1962.

Polynitro Aliphatic Nitramines

MILTON B. FRANKEL[1] and KARL KLAGER
Chemical Division of Aerojet-General Corp., Azusa, Calif.

THE MANNICH condensation of 2,2-dinitro-1-alkanols with ammonia was shown to give *bis*-substituted amines (*1*). This reaction has now been extended to include polynitro aliphatic primary amines and diamines, which were prepared by the acid hydrolysis of the corresponding isocyanates (*3*). The free amines were not isolated but generated in situ from the corresponding hydrochloride salts. Thus, adding an equivalent amount of sodium acetate or sodium hydroxide to an aqueous solution of the alcohol and amine hydrochloride at ambient temperature caused the condensation product to precipitate. The Mannich condensation products were yellow oils or solids of limited stability and difficult to purify. Nitration of this secondary amine with a mixture of absolute nitric acid and acetic anhydride at 5 to 10° C. or with a mixture of absolute nitric acid and concentrated sulfuric acid at 50 to 55° C. gave the corresponding nitramine. The N-nitro derivatives are stable, easily crystallizable white solids; they are sensitive to impact and should be handled with care. The compounds prepared are summarized in Table I, many of these compounds were disclosed in a series of patents (*3*).

EXPERIMENTAL

1,1,1,6,6,6-Hexanitro-3-azahexane. This preparation was typical of the condensation of 2,2-dinitro-1-alkanols and polynitroalkyl amines. An 88-ml. quantity of 1.136*N* sodium hydroxide solution (0.10 mole) was added dropwise at room temperature to a stirred solution of 23.1 grams (0.10 mole) of 3,3,3-trinitropropyl amine hydrochloride, 18.1 grams (0.10 mole) of 2,2,2-trinitroethanol, and 150 ml. of water. A yellow oil immediately separated; on cooling in an ice bath the oil solidified to a yellow solid. The product was collected, washed with water, and dried, 28.2 grams (79%), m.p. 62 to 65° C. Recrystallization from chloroform gave yellow needles, m.p. 64 to 65° C.

1,1,1,3,6,6,6-Heptanitro-3-azahexane. This preparation is typical of the nitration of the Mannich condensation

---

[1] Present address, Stanford Research Institute, Menlo Park, Calif.