Enthalpies of Combustion of Nine Organic Nitrogen Compounds Related to Petroleum

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Enthalpies of combustion measured by precision oxygen-bomb combustion calorimetry are given for nine organic nitrogen compounds selected as key compounds present in or related to petroleum. Enthalpies of formation in the condensed phase are derived. Enthalpies of vaporization for five of the compounds were derived from vapor-pressure measurements, and enthalpies of formation in the gaseous state are given for these five compounds.

Thermochemical properties of organic nitrogen compounds related to petroleum were studied at the Bureau of Mines, Bartlesville (Okla.) Energy Research Center as part of API Research Project 52c, "Thermodynamics of Nitrogen Compounds." The studies of the enthalpies of combustion of nine organic nitrogen compounds are described, and the results are summarized in this report.

EXPERIMENTAL

Apparatus and Procedures. The basic apparatus and procedures used by the Bureau for the combustion calorimetry of organic nitrogen compounds have been described (*7*, *9*, *16*). The calorimeter and bomb used for each compound, the benzoic acid sample used for calibration of the system and the value of ε(calor) obtained, and the auxiliary substance and fuse used are identified in Table I.

Three rotating-bomb calorimeters, laboratory designations BMR I (*10*), BMR II (*8*), and BMR III, were used. Calorimeter BMR III is essentially identical with BMR II. Rotation of the bomb was unnecessary for nitrogen compound combustion calorimetry. A platinum-lined bomb, laboratory designation Pt-3b (*6*), and a tantalum-lined bomb, laboratory designation Ta 1 (*17*), were used. The volumes of the bombs change slightly with changes of electrodes and internal fittings, and these changes are shown in Table I.

Three different standard samples of benzoic acid were used to calibrate the calorimetric system during these investigations, and the benzoic acid used for each nitrogen compound is indicated in Table I. The certified values of National Bureau of Standards Samples 39F, 39G, and 39H were 26.4294 ± 0.0026 int kj, 26.4338 ± 0.0026 abs kj, and 26.434 ± 0.003 abs kj per gram mass, respectively. Conversion to standard conditions (*11*) gives 6312.97 ± 0.62, 6312.97 ± 0.62, and 6313.02 ± 0.72 cal/g for $-\Delta Ec^\circ/M$, the energy of the idealized combustion reaction.

The auxiliary substances used were a hydrocarbon oil, empirical formula $CH_{1.894}$ and laboratory designation USBM-P3a, and a polyester, empirical formula $C_{10}H_8O_4$ (Table I). The value of $\Delta Ec^\circ/M$ for the oil was determined several times, and the value used for a particular nitrogen compound combustion experiment was obtained from a series of oil combustion experiments chronologically near those with the nitrogen compound. Values of $\Delta Ec^\circ/M$ for the oil are listed in Table I. The amount of oil used as kindling material is ordinarily 20–50 mg, and inspection of the values of $\Delta Ec^\circ/M$ for the oil given in Table I shows that little or no error would have been introduced if the same value of $\Delta Ec^\circ/M$ had been used throughout. The value of $\Delta Ec^\circ/M$ for the polyester, obtained in experiments chronologically near those with indole and 2,3-dimethylindole, was −5473.89 ± 0.28 cal/g.

Two materials were used as fuses, cotton thread of empirical formula $CH_{1.774}O_{0.887}$ and filter paper of empirical formula $CH_{1.686}O_{0.843}$ (Table I).

For each experiment, 1 ml of distilled water was added to the bomb. The bomb was charged to 30 atm with pure oxygen (except for isoquinoline when the initial pressure was 30.66 atm).

Nitric acid was determined in the combustion products of all experiments (*9*, *16*), and carbon dioxide was determined in the combustion products for three or four experiments with each compound.

Borosilicate glass ampules confined the samples of all liquid compounds. Bags of polyester film confined the crystalline samples of indole and 2,3-dimethylindole. The low volatility of 9-methylcarbazole made sample confinement unnecessary, and pellets of this compound were burned.

For all of the compounds except isoquinoline, the combustion reaction was started near 23°C, and because of the masses of combustibles chosen, the final temperatures were nearly 25°C, the operating temperature of the isothermal jacket of the calorimeter. Isoquinoline freezes near 25°C, and the normal 23–25°C temperature rise was impractical, so the experimental measurements were started near 29°C and concluded at 31°C. The isothermal jacket was controlled at 31°C for these experiments, and the results obtained for isoquinoline refer to the liquid at 31°C.

Materials. All samples were from materials purified for the API Standard Sample Repository (American Petroleum Institute Research Project 58 at Carnegie-Mellon University) by the Bureau of Mines Laramie Energy Research Center.

Table II gives values of purity for all nine samples. Purities of six of the compounds were estimated from freezing temperature vs. fraction melted curves observed by the Low-Temperature Calorimetry Group at the Bartlesville Energy Research Center. Purities of three other compounds were estimated by gas-liquid chromatography and spectroscopy at the Bureau of Mines Laramie Energy Research Center. Carbon dioxide was determined in the combustion products, and these determinations are summarized in Table II. The quantitative carbon dioxide recoveries are an excellent indication of the purity and dryness of the materials, but isomeric impurity would not be shown.

The samples of 4-methylpyridine, piperidine, 2-methylpiperidine, and 2,5-dimethylpyrrole were dried by passing the vapor over freshly activated molecular sieve. 1-Methylpyrrole was dried by liquid contact with CaH_2. Pellets of indole, 2,3-dimethylindole, and 9-methylcarbazole were prepared from the standard samples as received. The material was opened and pelleted under dry nitrogen. Sealed polyester bags confined the samples of indole and 2,3-dimethylindole. The samples of 9-methylcarbazole were not confined. Pellets of 9-methyl-

Table I. Identification of Calorimetric System and Auxiliary Materials

	Calorimeter	Bomb (Vol, *L*)	Benzoic acid	ε(calor),[a] cal/deg	Auxiliary substance	$\Delta Ec°/M$(aux),[a] cal/g	Fuse material	$\Delta Ec°/M$ (fuse), cal/g
4-Methylpyridine	BMR III	Pt-3b(0.3494)	39H	4026.48 ± 0.31 (*8*)[b]	Oil	−10983.83 ± 0.69	Thread	−4050
Piperidine	BMR III	Ta 1 (0.3440)	39F	4017.46 ± 0.11 (*6*)	Oil	−10984.12 ± 0.51	Thread	−4050
2-Methylpiperidine	BMR III	Pt-3b(0.3494)	39H	4026.48 ± 0.31 (*8*)	Oil	−10983.83 ± 0.69	Thread	−4050
1-Methylpyrrole	BMR I	Pt-3b(0.3501)	39G	3899.86 ± 0.18 (*6*)	Oil	−10983.70 ± 0.29	Paper	−3923
2,5-Dimethylpyrrole	BMR III	Pt-3b(0.3494)	39H	4026.48 ± 0.31 (*8*)	Oil	−10983.83 ± 0.69	Thread	−4050
Indole	BMR II	Pt-3b(0.3494)	39H	4007.91 ± 0.07 (*8*)	Polyester	−5473.89 ± 0.28	Thread	−4050
2,3-Dimethylindole	BMR II	Pt-3b(0.3494)	39H	4007.91 ± 0.07 (*8*)	Polyester	−5473.89 ± 0.28	Thread	−4050
9-Methylcarbazole	BMR III	Ta 1 (0.3440)	39F	4017.46 ± 0.11 (*6*)	...[c]	...	Thread	−4050
Isoquinoline	BMR II	Pt-3b(0.3494)	39H	4009.83 ± 0.15 (*6*)	Oil	−10983.83 ± 0.69	Thread	−4050

[a] Mean value with standard deviation. [b] Number of experiments. [c] No auxiliary material was used.

Table II. Compound Description

				Physical properties[a]		
Compound	Formula	Purity	CO_2 recovery	ρ, g/ml	$(\partial E/\partial P)_T$, cal/atm/g	c_p, cal/g/deg
4-Methylpyridine	C_6H_7N	99.97[b]	99.99 ± 0.01	0.95037	−0.0073	0.407[c]
Piperidine	$C_5H_{11}N$	99.94[b]	100.01 ± 0.01	0.85664	−0.0092	0.505
2-Methylpiperidine	$C_6H_{13}N$	99.87[b]	99.99 ± 0.01	0.83519	−0.0098	0.513
1-Methylpyrrole	C_5H_7N	99.998[b]	100.02 ± 0.02	0.90469	−0.0087	0.442
2,5-Dimethylpyrrole	C_6H_9N	99.90[b]	100.00 ± 0.01	0.93224	−0.0066	0.491
Indole	C_8H_7N	(99.9 ± 0.1)[d]	99.99 ± 0.01	1.186	(−0.0028)[e]	(0.289)
2,3-Dimethylindole	$C_{10}H_{11}N$	(99.9 ± 0.1)	99.99 ± 0.01	1.104	(−0.0028)	(0.289)
9-Methylcarbazole	$C_{13}H_{11}N$	99.995[b]	100.01 ± 0.01	1.429	(−0.006)	0.287
Isoquinoline	C_9H_7N	(99.9 ± 0.1)[d]	100.00 ± 0.03	1.091	(−0.0028)	(0.35)

[a] Values for 298.15°K except for isoquinoline at 304.15°K. [b] Purity estimated from freezing temperature versus fraction melted curves by Low-Temperature Calorimetry Group at Bartlesville Energy Research Center. [c] Heat capacities from Low-Temperature Calorimetry Group at Bartlesville Energy Research Center. [d] Purity estimated by API Project 52 (Laramie Energy Research Center) from gas-liquid chromatography and spectral data. [e] Values in parentheses are estimates.

Table III. Summary of Typical Calorimetric Experiments

	298.15°K								
	4-Methylpyridine	Piperidine	2-Methylpiperidine	1-Methylpyrrole	2,5-Dimethylpyrrole	Indole	2,3-Dimethylindole	9-Methylcarbazole	304.15°K, Isoquinoline
m' (compd), g	0.89551	0.79014	0.80920	0.81637	0.85292	0.863250	0.829567	0.90254	0.888990
m'' (oil), g	0.03697	0.03299	0.02615	0.05727	0.04535	...	...	...	0.026526
m''' (polyester), g	...	...	...	...	...	0.089285	0.089794	...	...
m'''' (fuse), g	0.00090	0.00119	0.00138	0.00399	0.00121	0.001252	0.001149	0.00107	0.000937
$\Delta t_c = t_f - t_i + \Delta t_{corr}$	2.05368	1.99660	2.05352	2.03513	2.05582	1.98477	2.00072	2.01462	1.99595
ε (calor)($-\Delta t_c$), cal	−8269.10	−8021.26	−8268.46	−7936.72	−8277.72	−7954.78	−8018.70	−8093.66	−8003.42
ε (cont)($-\Delta t_c$), cal	−10.26	−9.91	−10.38	−10.04	−10.35	−9.52	−9.58	−8.75	−9.94
ΔE_{ign}, cal	0.67	1.05	0.67	1.35	0.57	0.71	0.59	2.13	0.43
ΔE_{dec}, HNO_3, cal	10.91	13.34	12.37	15.26	11.05	11.33	9.12	11.44	9.09
$\Delta E_{corr\ to\ std\ states}$, cal	4.10	2.22	2.34	3.42	3.49	4.87	4.43	4.84	4.58
$-m''\Delta Ec°/M$(oil), cal	406.07	362.37	287.23	629.04	498.12	...	...	...	291.25
$-m'''\Delta Ec°/M$(polyester), cal	...	...	...	...	...	488.74	491.52	...	...
$-m''''\Delta Ec°/M$(fuse), cal	3.65	4.82	5.59	15.65	4.90	5.07	4.65	4.34	3.79
$m'\Delta Ec°/M$(compd), cal	−7853.96	−7647.37	−7970.64	−7282.04	−7769.94	−7453.58	−7517.97	−8079.66	−7704.22
$\Delta Ec°/M$(compd), cal, g^{-1}	−8770.38	−9678.50	−9850.03	−8920.02	−9109.81	−8634.32	−9062.52	−8952.14	−8666.26

carbazole were exposed to the laboratory atmosphere (50% relative humidity), and no change of weight could be detected over 4-hr weighing intervals.

For reducing weights in air to masses and converting the energy of the actual bomb process to that of the isothermal process and reducing to standard states (*11*), the values summarized in Table II were used for density, ρ, the change of internal energy with pressure, $(\partial E/\partial P)_T$, and heat capacity, c_p. Research of API Project 52 at the Bureau of Mines Laramie Research Center gave values of density and the temperature dependence of density for five of the compounds. Values of $(\partial E/\partial P)_T$ were calculated form the temperature dependence of density by using the approximation, $(\partial E/\partial P)_T = -T(\partial V/\partial T)_P$. For the remaining four compounds, values of density were obtained by weighing a pellet or ampule of known volume.

Units of Measurements. The experimental results are based on the 1961 atomic weights (*2*) and the 1963 definition of the thermochemical calorie (1 cal = 4.184 J) (*3*). The reference temperature was 25°C for all compounds except isoquinoline for which the reference temperature was 31°C.

Calorimetric Results. Typical combustion experiments for each of the nine compounds are summarized in Table III. It is impractical to list summaries for all experiments, but values of $\Delta Ec°/M$ for all experiments are given in Table IV.

Table IV. Summary of Experimental Results. Values of $\Delta Ec°/M$ in Cal/G

	298.15°K								
	4-Methyl-pyridine	Piperidine	2-Methyl-piperidine	1-Methyl-pyrrole	2,5-Dimethyl-pyrrole	Indole[a]	2,3-Dimethyl-indole[a]	9-Methyl-carbazole[a]	304.15°K, Isoquinoline
	−8774.16	−9678.50	−9845.10	−8920.02	−9109.81	−8634.32	−9063.71	−8952.14	−8666.26
	−8772.18	−9677.72	−9851.33	−8920.28	−9107.57	−8633.93	−9062.63	−8950.69	−8666.25
	−8771.27	−9676.02	−9851.68	−8919.32	−9108.48	−8633.31	−9062.08	−8950.82	−8665.69
	−8769.56	−9676.72	−9848.02	−8919.44	−9110.24	−8633.96	−9062.25	−8950.87	−8664.91
	−8768.73	−9675.54	−9850.80	−8919.06	−9110.66	−8634.66	−9061.48	−8950.78	−8664.97
	−8768.73	−9677.73	−9849.88	−8918.39	−9109.44	−8634.21	−9063.05	−8951.02	−8666.60
	−8771.26	−9676.83	−9851.45		−9107.55	−8632.88	−9062.07		−8667.77
	−8770.38		−9850.03		−9108.55	−8634.48	−9062.52		
Mean	−8770.78	−9677.01	−9849.79	−8919.42	−9109.04	−8633.97	−9062.47	−8951.05	−8666.06
Std dev	±0.65	±0.39	±0.79	±0.28	±0.42	±0.21	±0.24	±0.22	±0.38

[a] Values of $\Delta Ec°/M$ are crystalline state.

Table V. Molal Values for Condensed State

Compound	State	T, °K	$\Delta Ec°$, kcal/mol	$\Delta Hc°$, kcal/mol	$\Delta Hf°$, kcal/mol
4-Methylpyridine	Liquid	298.15	−816.82 ± 0.20	−817.56 ± 0.20	14.15 ± 0.21
Piperidine	Liquid	298.15	−824.00 ± 0.12	−825.33 ± 0.12	−20.66 ± 0.14
2-Methylpiperidine	Liquid	298.15	−976.87 ± 0.24	−978.50 ± 0.24	−29.86 ± 0.26
1-Methylpyrrole	Liquid	298.15	−723.53 ± 0.10	−724.27 ± 0.10	14.91 ± 0.12
2,5-Dimethylpyrrole	Liquid	298.15	−866.68 ± 0.18	−867.72 ± 0.18	−4.01 ± 0.20
Indole	Crystalline	298.15	−1011.48 ± 0.15	−1012.22 ± 0.15	20.71 ± 0.18
2,3-Dimethylindole	Crystalline	298.15	−1315.92 ± 0.19	−1317.25 ± 0.19	1.01 ± 0.23
9-Methylcarbazole	Crystalline	298.15	−1622.28 ± 0.20	−1623.61 ± 0.20	25.22 ± 0.25
Isoquinoline	Liquid	304.15	−1119.33 ± 0.18	−1120.09 ± 0.18	34.68 ± 0.21

All values of $\Delta Ec°/M$ in Tables III and IV refer to the generalized combustion Reaction 1:

$$C_aH_bN_c\ (\mathrm{l\ or\ c}) + (a + b/4)O_2(g) = aCO_2(g) + (b/2)H_2O(l) + (c/2)N_2(g) \quad (1)$$

Table V gives derived molal values of $\Delta Ec°$, the energy of the idealized combustion reaction; $\Delta Hc°$, the standard enthalpy of combustion; and $\Delta Hf°$, the standard enthalpy of formation. Values of $\Delta Ec°$ and $\Delta Hc°$ refer to Reaction 1. The values of $\Delta Hf°$ refer to Reaction 2:

$$aC\ (\mathrm{c, graphite}) + b/2H_2(g) + c/2N_2(g) = C_aH_bN_c\ (\mathrm{l\ or\ c}) \quad (2)$$

Uncertainties given in Table V are the "uncertainty interval" (*13*). The enthalpies of formation of gaseous CO_2 and liquid H_2O were taken to be −94.051 and −68.315 kcal/mol, respectively (*19*). Uncertainties assigned to gaseous CO_2(*15*) and liquid H_2O (*14*) were 0.011 and 0.010 kcal/mol, respectively.

Enthalpy of Formation in Gaseous State. Vapor-pressure measurements were reported for five of the compounds (*12*). Values of the enthalpy of vaporization at 298.15°K were computed from the Cox equations (*4*, *12*), the exact form of the Clapeyron equation, and estimated values of the second virial coefficient. These values of the enthalpy of vaporization (Table VI) are strictly the enthalpy of vaporization to the real gas, $\Delta Hv_{298.15}$, but are not significantly different from the standard enthalpy of vaporization, $\Delta Hv°_{298.15}$. The enthalpies of vaporization were combined with the enthalpy of formation in the condensed state to obtain the enthalpy of formation in the ideal gaseous state, Table VI, Reaction 3:

$$aC(\mathrm{c, graphite}) + b/2H_2(g) + c/2N_2(g) = C_aH_bN_c(g) \quad (3)$$

Table VI. Enthalpy of Vaporization and Enthalpy of Formation of Ideal Gas at 298.15°K

Compound	$\Delta Hv°$, kcal/mol	$\Delta Hf°(g)$, kcal/mol
4-Methylpyridine	10.65 ± 0.05	24.80 ± 0.22
Piperidine	9.39 ± 0.05	−11.27 ± 0.15
2-Methylpiperidine	9.67 ± 0.05	−20.19 ± 0.27
1-Methylpyrrole	9.74 ± 0.05	24.65 ± 0.13
2,5-Dimethylpyrrole	13.51 ± 0.05	9.50 ± 0.21

Table VII. Comparison of Enthalpies of Combustion at 298.15°K, kcal/mol

Compound	State	$-\Delta Hc°$ (lit)	$-\Delta Hc°$ (this research)
4-Methylpyridine	Liquid	816.99 ± 0.30[a]	817.56 ± 0.20
Piperidine	Liquid	824.94 ± 0.56[b]	825.33 ± 0.12
Indole	Crystalline	1019.4 ± 1.0[c]	1012.22 ± 0.15

[a] Reference *5*. [b] Reference *1*. [c] Reference *18*.

DISCUSSION

In a comparison with the literature, three of the compounds had been studied previously (*1*, *5*, *18*), and the older literature values of the enthalpy of combustion are compared in Table VII with the values obtained in this research.

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NOMENCLATURE

∂ = differential operator
m = mass, grams
n = number of moles
P = pressure, atm
T = temperature, °K
ε (calor) = heat equivalent of calorimeter, cal/°K
ε (cont) = heat equivalent of contents, cal/°K
ΔE_{dec} = energy of decomposition, cal
ΔE_{ign} = electrical ignition energy, cal
$\Delta E_{\text{cor to std states}}$ = energy for reduction to standard states, cal
$\Delta Ec°$ = standard energy of idealized combustion reaction, kcal/mol
$\Delta Hc°$ = standard enthalpy of combustion, kcal/mol
$\Delta Hf°$ = standard enthalpy of formation, kcal/mol
$\Delta Hv°$ = standard enthalpy of vaporization, kcal/mol

SUBSCRIPTS

i = initial state
f = final state

LITERATURE CITED

(1) Bedford, A. F., Beezer, A. E., Mortimer, C. T., *J. Chem. Soc.*, **1963**, p 2039.
(2) Cameron, A. E., Wichers, E., *J. Amer. Chem. Soc.*, **84**, 4175 (1962).
(3) Cohen, E. R., DuMond, J. W. M., *Rev. Mod. Phys.*, **37**, 537 (1965).
(4) Cox, E. R., *Ind. Eng. Chem.*, **28**, 613 (1936).
(5) Cox, J. D., Challoner, A. R., Meetham, A. R., *J. Chem. Soc.*, **1964**, p 265.
(6) Good, W. D., Douslin, D. R., Scott, D. W., George, A., Lacina, J. L., Dawson, J. P., Waddington, G., *J. Phys. Chem.*, **63**, 1133 (1959).
(7) Good, W. D., Moore, R. T., *J. Chem. Eng. Data*, **15**, 150 (1970).
(8) Good, W. D., Scott, D. W., Waddington, G., *J. Phys. Chem.*, **60**, 1080 (1956).
(9) Hubbard, W. N., Frow, F. R., Waddington, G., *ibid.*, **65**, 1326 (1961).
(10) Hubbard, W. N., Katz, C., Waddington, G., *ibid.*, **58**, 142 (1954).
(11) Hubbard, W. N., Scott, D. W., Waddington, G., "Experimental Thermochemistry," F. D. Rossini, Ed., Chap. 5, pp 75-128, Interscience, New York, N.Y., 1956.
(12) Osborn, A. G., Douslin, D. R., *J. Chem. Eng. Data*, **13**, 534 (1968).
(13) Rossini, F. D., "Experimental Thermochemistry," F. D. Rossini, Ed., Chap. 14, pp 297-320, Interscience, New York, N.Y., 1956.
(14) Rossini, F. D., *J. Res. Natl. Bur. Std.*, **6**, 1 (1931).
(15) Rossini, F. D., Jessup, R. S., *ibid.*, **21**, 491 (1938).
(16) Smith, N. K., Good, W. D., *J. Chem. Eng. Data*, **12**, 572 (1967).
(17) Smith, N. K., Scott, D. W., McCullough, J. P., *J. Phys. Chem.*, **68**, 934 (1964).
(18) Stern, A., Klebs, G., *Ann. Chim.*, **500**, 91 (1932).
(19) Wagman, D. D., Evans, W. H., Halow, I., Parker, V. B., Bailey, S. M., Schumm, R. H., "Selected Values of Chemical Thermodynamic Properties," *Natl. Bur. Std. (U.S.) Tech. Note*, **270-3** (1968).

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Phase Studies of Some Nitroalkane Hydocarbon Mixtures

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Upper critical solution temperatures were determined for the solutions nitroethane–*n*-decane, ~58°C; nitroethane–*n*-nonane, 49.5°C; nitroethane–*n*-hexane, 32.5°C; nitroethane–cyclohexane, 25°C; nitroethane–methylcyclohexane, 25°C; 2-nitropropane–*n*-nonane, —4.5°C; nitromethane–1,3,5-trimethylbenzene, —16°C; and nitromethane–1,2,4-trimethylbenzene, —31°C. No liquid-liquid immiscibility was observed in benzene solutions of nitromethane, nitromethane-d_3, nitroethane, 1-nitropropane, or 2-nitropropane. The benzene–2-nitropropane system was determined to be a simple eutectic at a temperature of —98°C and composition of 0.93 mole fraction 2-nitropropane. Cooling curve measurements on benzene solutions of nitromethane and nitromethane-d_3 indicate they form simple eutectics.

Several cases of liquid-liquid immiscibility were observed in connection with our work on the excess Gibbs energy of mixing (*1*) and on the surface tension of nitroalkane–hydrocarbon solutions. This paper reports an extension of these observations to eight nitroalkane hydrocarbon solutions for which upper critical solution temperatures (UCST) were determined. Also reported are some freezing and eutectic temperatures determined from cooling curves of solutions of benzene with nitromethane, nitromethane-d_3, and 2-nitropropane.

EXPERIMENTAL

Chemicals. The nitroalkanes were purified by drying over calcium sulfate followed by distillation under reduced pressure. Nitromethane, Fisher reagent grade, distilled at 60°C and 183 torr; nitroethane, Matheson, Coleman and Bell practical grade, distilled at 57°C and 97 torr, 2-nitropropane, Eastman practical grade distilled at 60°C and 100 torr. Boiling points and densities checked satisfactorily with literature values (*13*). Nitromethane-d_3, Dia-

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