Taft and Smith[4] determined the rates of reaction of DDM in ethanol at 25° with thirteen carboxylic acids and found a $\rho^*$ value of 1.175 ± 0.043. The relatively larger $\rho^*$ value of 2.80 found in the present study for the reaction in toluene at 25° may be helpful in determining more accurately small differences in polarity.

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[CONTRIBUTION FROM THE ALLEGANY BALLISTICS LABORATORY,[1] HERCULES POWDER COMPANY]

# Burning Rates of Deuterated Nitrate Esters

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Several deuterated nitrate esters have been prepared and their burning rates measured. The results are in agreement with the hypothesis that the diffusion of atomic hydrogen is an important mechanism of energy feedback in these flames and that the principal initial reaction involves attack by atomic hydrogen on nitrate ester.

Previous work on temperature profiles of burning liquid nitrate esters[2] has shown that the temperature and the temperature gradients at the liquid–gas interface are very low. In view of the somewhat different interpretation of quite similar data by others[3] it must be recognized that this experimental result cannot be accepted at present without some reservation. Nevertheless, considerable doubt has been thrown on a widely accepted mechanism of propagation of the combustion front. According to this mechanism,[4] heat is transmitted from the hot combustion gases to the surface of the condensed phase by conduction and radiation, and heat is also generated in the top layer of the condensed phase by exothermic decomposition reactions. The resulting high temperature in the surface layer is supposed to lead to gasification by decomposition or volatilization.

Our evidence indicated that the surface temperatures were too low to account for the observed rate of burning on the basis of the thermal mechanism. Therefore it was decided to examine another mechanism. involving attack by free radicals on the nitrate ester. Such a scheme emphasizes the role of diffusion of matter rather than of heat as a method of energy transport in flame propagation, inasmuch as the free radicals must be formed in the hot part of the flame and must diffuse back through the intermediate gases to the liquid surface. This type of mechanism has received considerable attention in the field of gaseous flames.[5] To our knowledge it has not been considered seriously in previous work on solid or liquid fuels.

Of the possible free radicals which might attack the nitrate ester the one which diffuses most readily and therefore is the most likely active species is atomic hydrogen. The substitution of deuterium for hydrogen should thus have a pronounced retarding effect on the burning rate. In order to test this scheme, several deuterated nitrate esters have been prepared and their burning rates measured. The results are in qualitative agreement with expectations based on the free radical hypothesis.

## Experimental

**Materials.**—The deuterated starting materials were obtained at an isotopic purity of 95% or better from a commercial supplier.[6] The preparations followed the general course: alcohol → halide → nitrate and were found to proceed without appreciable exchange.

**Ethyl Nitrate-$d_5$.**—A mixture of 0.5 g. (16 meq.) of red phosphorus, 1.66 g. (31.9 mmoles) of ethyl alcohol-$d_6$, and 4.3 g. (33.9 meq.) of resublimed iodine was refluxed for 2.5 hr. The deuterated ethyl iodide produced in this reaction was distilled into a cooled flask containing 1.5 g. of potassium carbonate and a small amount of mercury. (Potassium carbonate to repress acidity, mercury to remove excess iodine.) 8.5 g. of silver nitrate (50 mmoles) was added slowly, while the flask was cooled in an ice-bath. The mixture was refluxed for 2 hr., and the crude nitrate was distilled into a flask containing 1.5 g. of potassium carbonate and a droplet of mercury. A small amount of calcium sulfate was added to remove cloudiness (presumably water). A further 7.5 g. (44 mmoles) of silver nitrate was added and the mixture again refluxed for 2 hr. The product was distilled into a cooled tube equipped with a drying tube. The yield was 2.41 g., 83% of theory. (The drying precautions were not observed with the first preparation, samples from which were used for elemental analysis and one mass spectrometric analysis.)

**Physical properties:** $n^{25}$D 1.3807, b.p. 87.8–88.0° (cor.).

*Anal.*[7] Calcd. for $C_2D_5O_3N$ (98% enrichment level): C, 25.06; H + D, 10.25; N, 14.61. Found: C, 24.56; H + D, 9.68; N, 14.18.

**Mass Spectrometric Analysis.**[8]—Direct analysis of the mass spectrum showed that the sample contained approximately 90% completely deuterated material, 3% with one hydrogen atom per molecule, and a maximum of 5 mole per cent. water. A subsequent analysis of the pyrolysis products indicated a maximum water content of 4 mole per cent. and a minimum enrichment level of 98%.

An unusual, though not unique, feature of the mass spectrum is that the highest mass peak observed contains one hydrogen (or deuterium) atom less than the parent molecule.

**Infrared Analysis.**[9]—Infrared spectra were obtained for both liquid and vapor and showed the expected shift of the C–H stretching bands. This shift uncovered a previously unnoticed band at 2920 cm.$^{-1}$, which appears to be a combination band of the 1640 and 1280 cm.$^{-1}$ nitrate frequencies.[10]

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[1] A facility owned by the U. S. Government and operated for the U. S. Navy, Bureau of Ordnance, by Hercules Powder Company under Contract NOrd 10431.

[2] R. Steinberger and K. E. Carder, *J. Phys. Chem.*, **59**, 255 (1955).

[3] D. L. Hildenbrand, A. G. Whittaker and C. B. Euston, *ibid.*, **58**, 1130 (1954).

[4] (a) S. F. Boys and J. Corner, *Proc. Roy. Soc.* (*London*), **A197**, 90 (1949); (b) O. K. Rice and R. Ginell, *J. Phys. Colloid Chem.*, **54**, 885 (1950); (c) R. G. Parr and B. L. Crawford, Jr., *ibid.*, **54**, 929 (1950); (d) W. P. Reid, *ibid.*, **57**, 242 (1953).

[5] M. W. Evans, *Chem. Revs.*, **51**, 363 (1952).

[6] Tracerlab, Inc., Boston, Mass.

[7] Micro-Tech Laboratories, Skokie, Ill. Values of %H as received were recalculated on the basis of a 98% enrichment level.

[8] Mass spectrometric analyses were performed by Dr. C. A. Genge, Hercules Experiment Station, Wilmington, Del.

[9] Infrared spectra were measured by R. W. Phillips, this Laboratory.

[10] We are indebted to Dr. Bryce L. Crawford, Jr., University of Minnesota, for this suggestion.

**Ethylene Glycol Dinitrate-$d_4$.**—The method of Ferris and co-workers[11] was used, the starting material being deuterated ethylene bromide. Ten g. of the bromide (52 mmoles) was added to a solution of 35 g. (206 mmoles) of silver nitrate in 50 ml. of acetonitrile. The solution was heated at 70–75° for 2 hr. and the product isolated by filtration, washing and evaporation of the solvent. The product was used without further distillation, since runs with ordinary ethylene bromide had shown the purity of the resulting nitrate to be equal to that of a distilled sample, as measured by infrared spectroscopy and refractive index. The yield was 7.18 g., 88.5% of theory, $n^{24}$D 1.4445. Mass spectrometric analysis showed the sample to have an isotopic purity of 96%. Infrared results were quite similar to those obtained with deuterated ethyl nitrate.

**Isopropyl Nitrate.**—The ordinary compound and three labeled varieties, 2-*d*-2-nitratopropane, 1,1,1,3,3,3-$d_6$-2-nitratopropane, and 2-nitratopropane-$d_7$, were prepared from the corresponding alcohols. To a mixture of 5 g. (83 mmoles) of alcohol and 1 g. (13 mmoles) of pyridine, chilled in an ice-bath, was added dropwise 10–11 g. (111–122 meq.) of phosphorus tribromide. The mixture was then refluxed until HBr fumes ceased to be evolved (1–2 hr.). Distillation and washing of the bromide gave a yield of 68–73% of the theoretical.

To the bromide, chilled in an ice-bath, finely pulverized silver nitrate in 75–100% excess was added very slowly. On completion of the addition, the mixture was warmed slowly and distilled at reduced pressure (*ca.* 100 mm.). A small amount of silver nitrate was placed in the receiver and a second distillation was carried out to obtain a pure product.

**Physical properties:** $CH_3CHONO_2CH_3$—$n^{25}$D 1.3882, $d^{20}_4$ 1.043, b.p. 101.7° (cor.); $CH_3CDONO_2CH_3$—$n^{25}$D 1.3876, $d^{20}_4$ 1.047, b.p. 101.2°; $CD_3CHONO_2CD_3$—$n^{25}$D 1.3854, $d^{20}_4$ 1.098, b.p. 100.4°; $CD_3CDONO_2CD_3$—$n^{25}$D 1.3849, $d^{20}_4$ 1.095, b.p. 99.7°.

Mass spectrometric analysis in this case showed enrichment levels far below those anticipated. However, the infrared spectra showed the expected changes due to partial and complete deuteration. Lack of sample precluded resolution of this discrepancy. However, in view of the lack of ambiguity of the spectra, the absence of exchange in the other nitrate esters prepared, and the substantial burning rate effects obtained, it is believed that the compounds are essentially the ones desired.

**Burning Rate Apparatus.**—The liquids were burned in 3 mm. i.d. Pyrex tubes in a window bomb under an atmosphere of nitrogen. Two methods were used for timing. In the first method, the tube was set up next to a template notched at 1/8" intervals, and the progress of the liquid surface down the tube was recorded photographically. The camera speed was calibrated by photographing a clock. In the second method, the tube was placed in contact with two thermocouples spaced one inch apart. The voltage generated by passage of the burning front past the thermocouples was used to start and stop a clock. The two methods gave identical results. Ignition was produced by means of a hot wire dipping into the liquid. In the case of the isopropyl nitrates it was found advantageous to introduce a plug of fibrous nitrocellulose into the top of the tube to aid ignition.

All burning rates, except those of the isopropyl nitrates, were obtained at a room temperature of 25 ± 2°, but the bomb was not thermostated. For the isopropyl nitrates, the bomb temperature was controlled at 50 ± 1° by means of a pyrometrically controlled electric heater.

## Results

The results of burning rate measurements are shown in Figs. 1–3. These may be summarized as follows.

**Ethyl Nitrate.**—The deuterated compound burned more slowly than the ordinary one by a factor of 1.4.

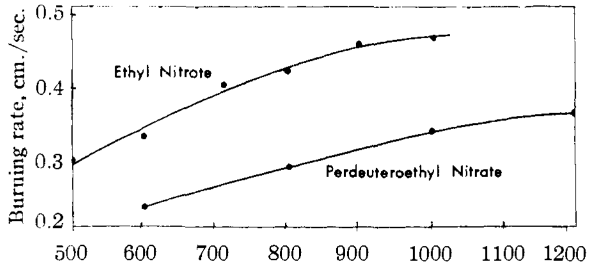

Fig. 1.—Burning rates of ordinary and deuterated ethyl nitrates.

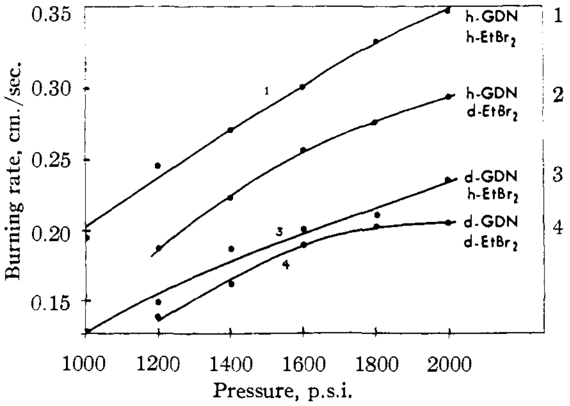

Fig. 2.—Burning rates of 1:1 molar mixtures of ordinary (h) and deuterated (d) ethylene glycol dinitrate (GDN) and ethylene bromide ($EtBr_2$).

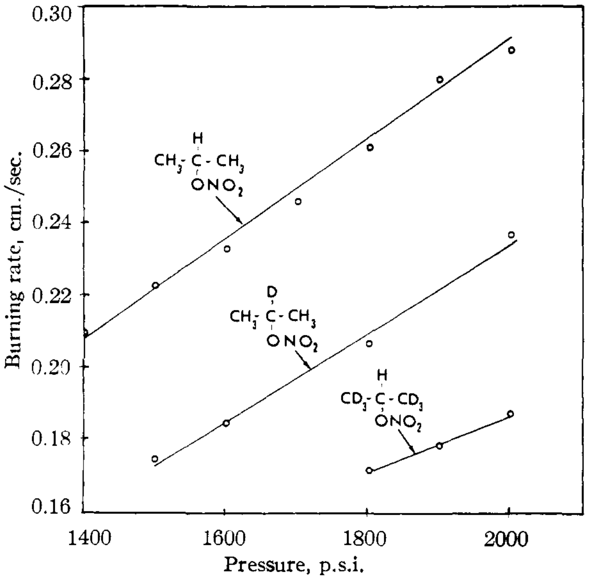

Fig. 3.—Burning rates of ordinary and deuterated isopropyl nitrates.

**Ethylene Glycol Dinitrate.**—This was burned as a 1:1 molar mixture with ethylene bromide. Four mixtures were tested, corresponding to the four possible combinations of deuterated and ordinary compounds. The completely deuterated mixture (no. 4) burned more slowly than the ordinary one (no. 1) by a factor of 1.7. The two partially deuterated mixtures (no. 2 and 3) burned at intermediate rates; the one containing deuterated nitrate and ordinary bromide (no. 3) burned more slowly than the one containing ordinary nitrate and deuterated bromide (no. 2).

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[11] A. F. Ferris, K. W. McLean, I. G. Marks and W. D. Emmons, THIS JOURNAL, **75**, 4078 (1953).

**Isopropyl Nitrate.**—The singly deuterated compound 2-*d*-2-nitratopropane burned more slowly than the ordinary one by a factor of 1.26, while the compound labeled in the reverse manner, 1,1,1,3,3,3-$d_6$-2-nitratopropane, exhibited retardation by a factor of 1.54. It has not been found possible to burn the completely deuterated compound under our experimental conditions.

## Discussion

In attempting to interpret the results obtained in this study, it is useful to consider them from the point of view of both the free radical diffusion- and the heat transfer mechanism of burning.

1. **Free Radical Mechanism.**—The burning rate effects of isotopic substitution can be interpreted easily by postulating as the reaction leading to gasification of the fuel the abstraction of a hydrogen atom in the $\alpha$-position of the nitrate ester by means of atomic hydrogen

$$H + RR'CHONO_2 \longrightarrow H_2 + RR'\dot{C}ONO_2 \quad (1)$$

All the observations on deuterated compounds fall into a pattern established by this reaction.

a. **Effect of Diffusion.**—Reaction 1 demands that substitution of deuterium for hydrogen in the nitrate ester should lead to a reduction in burning rate by decreasing the diffusion rate of the atomic hydrogen. This reagent is thought to be generated in the hot part of the flame at some distance from the liquid surface, and its concentration at the surface will most certainly depend on its diffusion rate. The present results do show such an effect, as may be seen by comparing 1,1,1,3,3,3-$d_6$-2-nitratopropane with ordinary isopropyl nitrate and mixture 2 of the ethylene glycol dinitrate system with mixture 1. In both these cases the deuterated fuels are heavily substituted (86 and 50%), but the $\alpha$-position of the nitrate ester is unchanged. Thus the observed rate effects must be largely due to diffusion. (A chemical effect due to the attacking species being partially D instead of H cannot be ruled out entirely but is unlikely in view of the work of others.[12])

It should be pointed out that the presence of a substantial diffusion effect pinpoints atomic hydrogen as the attacking radical. If other free radicals, such as OH, $CH_3$, $NO_2$, etc., were important, any effect directly attributable to differences in diffusion velocity would be expected to be very small or zero.

b. **Effect of Chemical Reactivity.**—The bond being broken in reaction 1 is a carbon–hydrogen bond. One would therefore expect the usual effect of isotopic substitution on the rate of such a reaction. This effect is actually observed, as may be seen by comparing 2-*d*-2-nitratopropane with ordinary isopropyl nitrate and mixture 3 of the ethylene glycol dinitrate system with mixture 2. In these two comparisons the isotopic substitution level is very nearly (or, in the second case, entirely) the same, so that no diffusion effect is expected. However the $\alpha$-position of the nitrate ester is now labeled, and the anticipated rate decrease takes place.

The two effects are both active in the completely deuterated compounds, of course, so that these exhibit still lower rates.

2. **Heat Transfer Mechanism.**—In order to account for the present results on the basis of the older mechanism, it might be assumed that the rates of the thermal decomposition reactions leading to heat development in and near the surface layer would be lowered by the substitution of deuterium for hydrogen. Such an effect would not be expected for the initial decomposition, however, since the thermal decomposition of nitrate esters is generally conceded to occur at the O–$NO_2$ bond[13] and thus does not involve the breaking of a C–H bond. A secondary reaction often written for these systems is the attack of $NO_2$ on aldehydes, and this might be expected to show an isotopic effect. In the thermal breakdown of isopropyl nitrate, for instance, acetaldehyde is a likely intermediate, and the reaction between it and $NO_2$ might be affected by isotopic substitution on the carbonyl carbon atom. However, one would not expect then a lowered burning rate for 1,1,1,3,3,3-$d_6$-2-nitratopropane, in which the prospective carbonyl carbon atom is normally substituted. If, on the other hand, the primary breakdown of isopropyl nitrate yields acetone rather than acetaldehyde, then a rate effect due to the abstraction of hydrogen from acetone would be expected for 1,1,1,3,3,3-$d_6$-2-nitratopropane but not for 2-*d*-2-nitratopropane. Thus the data do not support a chemical effect due to secondary hydrogen-abstracting reactions.

One could also assume that the diffusivity of heat in the gas layer adjacent to the burning surface would be lowered by the replacement of hydrogen and its compounds by their deuterium analogs. However this is not in accord with the difference in burning rate observed between mixtures 2 and 3 of the ethylene glycol dinitrate–ethylene bromide system, in which the deuterium level is the same.

## Conclusion

From the above discussion it may be seen that the present data provide strong support for a free-radical mechanism of energy transport in nitrate ester flames and for the attack of atomic hydrogen on the nitrate ester as a kinetically important step in the reaction sequence. It does not appear fruitful at this time to speculate as to further steps in the combustion mechanism. It will be necessary first to obtain detailed information regarding the physical and chemical structure of these flames.

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(12) (a) H. W. Melville, *J. Chem. Soc.*, 1243 (1934); (b) H. I. Schiff and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1 (1951).

(13) J. B. Levy, THIS JOURNAL, **76**, 3254 (1954).