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Nitric Acid Oxidation of High-Density Polyethylene. Organic Chemical Aspects

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ABSTRACT: Preparative-scale nitric acid oxidation of bulk, high-density polyethylene has given high yields of nitrated α,ω-alkanedioic acids with molecular weights in the range 1300 to 3000 similar to products reported in the literature. The acids have polydispersity indexes of about 1.05–1.3 and thus are very nearly monodisperse. Carboxyl to nitro group ratios vary between about 6:1 and 1.6:1 depending on preparation conditions. Concentrated sulfuric acid converts the nitro groups to keto groups forming keto acids of unchanged molecular weight. Partial reduction of the keto groups can be achieved by the Clemmensen or Wolff–Kishner procedures. In some of the oxidation reactions, dinitroalkanedioic acids of molecular weight 400 to 500 were obtained; in these it is shown that the nitro groups are situated near the chain ends in positions α, β, or γ with respect to the carboxyl group.

The extensive work of Keller and his co-workers on the oxidation of polyethylene single crystals has done much to unravel the problem of fold surface structure in crystalline polyethylene.[2] In such oxidations, the amorphous chain folds at the periphery of the crystallites are severed and degraded back to the more resistant crystalline portions of the polymer.

Although some of the more recent work from Keller's laboratory used ozone as the oxidant,[3,4] most of the earlier work was done with fuming nitric acid[5,6] following similar previous studies by Palmer and Cobbold.[7] The products of the nitric acid oxidation were identified as nitrated, long-chain alkanoic acids,[6,8] and although some passing interest has been shown in chemical manipulation of such products as gel-permeation chromatography standards[9] or polymer intermediates,[10] most of the work in this area was done from a polymer physical structure viewpoint.

Thus, our attention was attracted to the organic chemistry of the process, its preparative aspects, and further characterization of the products.

Our characterization work in particular has clarified some inconsistencies in the literature and has led us to some further speculation on the course of the oxidation–nitration reaction.

Results and Discussion

Mechanics and Conditions of the Oxidation–Nitration Reaction. The nitric acid oxidations described in the literature were carried out on small amounts of carefully recrystallized polyethylene (0.1–0.3 g) in heated, sealed glass tubes and reaction times of 1 to 3 weeks.[5-10] Since our preparative work demanded large amounts of material, these limitations were unacceptable.

In preliminary experiments designed to permit larger scale development, several oxidations of high-density polyethylene pellets[11,12,13] were carried out on a 50-g scale in sealed rocker bombs. In general, these proceeded satisfactorily and gave products very similar to those of Keller et al. However, the potential explosion hazard of such systems, particularly if accidentally heated above the polymer melt temperature, encouraged us to explore the reaction in open vessels at atmospheric-pressure reflux temperatures. In this way, we were able to operate on a 200-g scale.

In most of the published work referred to, 95% fuming nitric acid was used although some was done with 82.5% acid.[4,8] Constant reaction temperatures of 60 or 80 °C were used. We worked with three different strengths of acid, namely, ordinary concentrated (71% HNO_3), 90% fuming, and red fuming

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Table I
Nitric Acid Oxidation of High-Density Polyethylenes,[a] Nitrated Alkanedioic Acids[b]

Prepn No.	Preparation conditions: Nitric acid type[c]	Stirring mode[d]	Time, h	Solids recovery, %[e]	GPC data: $\overline{M}_w$	$\overline{M}_n$	PI[f]	$\overline{M}_n$ titration	IR ratio[g] CO_2H/NO_2
1[h]	RF	Bomb	16	82	2400	1800	1.17		5.92
2	RF	Mag	96[i]	93	1700	1300	1.19	1350	5.19
3[j]	RF	Mag	60	99	2900	2100	1.26	1900	5.35
4	RF	Mech	90	97	4400	3100	1.27	2400	4.78
5	RF	Mech	24	92	7000	4100	1.27	3250	3.00
6	RF	Mech[k]	24	33	2800	2400	1.06	1900	2.65
7	F	Mag	60	91	3400	2600	1.16	2300	4.15
8	F	Mag	60	95	3600	2800	1.14	2400	3.86
9	F	Mag	60	95	2800	2300	1.07	2200	3.77
10	F	Mag	40	92	3800	2800	1.21	2350	3.21
11[j]	F	Mag	40	94	2400	1800	1.17	1700	3.98
12	F	Mech	60	33[l]	2200	1900	1.01	1700	2.74
13	F	Mech	48	26[m]	1900	1500	1.13	1800	2.56
14 F[n]	F	Mech	24	50 } 88	3300	2600	1.17	2000	3.25
14 P[n]				33	3700	2800	1.19	2300	3.06
15 F[n,o]	F	Mech	24	24 } 89	3400	2600	1.15	2150	3.40
15 P[n,o]				65	3800	2900	1.17	2350	3.07
16	Conc	Mag	60	56	2800	2400	1.05	1900	2.63
17	Conc	Mag	20	43[p]	2800	2000	1.24	2150	1.63

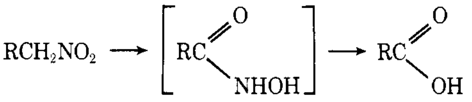
[a] Alathon 7040 polyethylene resin (see ref 12) except for preparation 15. [b] Elemental analyses not given because they are dominated by the hydrocarbon portion so that differences are not significant. [c] RF is red fuming, F is 90% fuming, and Conc is ordinary concentrated 71% HNO_3. [d] Mag is magnetic stirring and Mech is mechanical paddle stirring. [e] These are not percent yields but rather the ratio of weights of solid recovered to solid charged. [f] Polydispersity index, $\overline{M}_w/\overline{M}_n$, corrected for instrumental broadening. [g] 2% in KBr wafers, ratio of absorbance at 1708 cm^{-1} (CO_2H) to 1550 cm^{-1} (NO_2); see ref 21. [h] Closed bomb, 80 °C, autogenous pressure. This experiment by R. C. Ferguson. [i] Two stages; pellets oxidized 48 h, recrystallized from xylene, and oxidized 48 h more. [j] Recrystallized from xylene before oxidation. [k] Extra agitation caused by the thermometer inserted directly into the reaction mixture. Product accompanied by 31% nitro-carboxylic grease for which see Table II. [l] $\overline{M}_n$ = 2000, ebullioscopic in xylene. Solid accompanied by low yield of nitro-carboxylic grease. See Table II. [m] $\overline{M}_n$ = 1950, ebullioscopic in xylene. Solid accompanied by 21% nitro-carboxylic grease. See Table II. [n] Two solid constituents, fines (F) and pellets (P). [o] Starting material Alathon 7050 polyethylene resin. [p] Accompanied by 11% nitro-carboxylic grease.

nitric acid (>95% HNO_3). Since these acids were used at their reflux temperatures at atmospheric pressures, reaction temperatures were necessarily self-regulated within safe limits. However, since oxides of nitrogen are continuously lost under these conditions, the concentration of acid changes as does the reaction temperature. For example, with red fuming nitric acid, the initial reflux temperature was about 55–60 °C but increased to 90–100 °C after 24–48 h reaction time. These variations caused some difficulty with respect to reproducibility. Nevertheless, these different conditions afforded substantial variation in the products with respect to yield, molecular weight, and carboxyl to nitro group content. This contrasts with the closed systems which gave products relatively invariant in these respects.[6,8–10]

Moreover, we found that the degree of agitation of the reaction mixtures is an important determinant of product composition and yield. The importance of this factor is not evident from previously published work. Although not specified, these were presumably static systems and one infers from them that the major determinant of product character is the traverse length of molecules in the crystallites. However, Keller and Udagawa[8] have shown that state of subdivision and reaction time are also important factors.

Nature of the Products. Before discussing our products, it would be well to summarize the conclusions of Keller and co-workers.

In an early paper, they concluded that each stem end of their oxidized products possessed two oxygen atoms and therefore each molecule was terminated by either a carboxyl group or a nitro group.[6] Moreover, the carboxyl to nitro group ratio was about 11:1. In a later paper, these conclusions were sustained,[9a] and the notion that the nitro groups were terminal (primary) was reinforced by their *presumed* conversion to carboxyl groups on treatment with hot concentrated sulfuric acid. Indeed, such a transformation could occur by the well-known hydroxamic acid rearrangement and hydrolysis.[14]



On these bases, the original products would be a mixture of compositions such as **1**, **2**, and **3**. Because of the high carboxyl to nitro group ratio, contributions by **2** and **3** would be relatively small.

$HO_2C(CH_2)_nCO_2H$ **1**

$O_2NCH_2(CH_2)_nCO_2H$ **2**

$O_2NCH_2(CH_2)_nCH_2NO_2$ **3**

In a still later paper,[8] Keller and Udagawa modified their view and concluded that the chains were terminated solely by carboxyl groups but that the "function and position of the nitro group remains unknown", but they did not reconcile this revised view with their nitro group removal experiments. In separate and still later work, Ballard and Dawkins retained the view that the nitro groups were terminal and carried out the nitro group removal procedure on the assumption that they were generating uniform carboxylic acid bifunctionality.[10] As we shall see from the work described below, there is now no doubt that the oxidation products are at the outset terminated solely by carboxyl groups and that the nitro groups are indeed secondary.

In Table I are summarized the properties of our primary

Table II
Characterization of Nitro-Carboxylic Greases

Prepn No.	Source Table I prepn No.	Anal.								Titration[a] neut equiv		IR ratio CO_2H/NO_2[b]
			Calcd				Found					
		Formula	FW	% C	% H	% N	% C	% H	% N	1st	2nd	
1[c]	12	$C_{18}H_{32}N_2O_8$	404.5	53.4	7.9	6.9	53.2	7.8	6.9			
2[d]	13	$C_{21}H_{38}N_2O_8$	446.5	56.5	8.6	6.3	56.2	8.6	6.3	402	190	1.06
3[e]	17	$C_{21}H_{38}N_2O_8$	446.5	56.5	8.6	6.3	56.4	8.5	6.0	399	198	1.08
4[f]	6	$C_{22}H_{40}N_2O_8$	460.6	57.4	8.8	6.1	57.6	8.9	5.9	496	246	1.10

[a] Potentiometric in acetone with $(n\text{-Bu})_4NOH$ titrant. [b] Ratio of 1708 and 1550 cm^{-1} absorbances. Run neat. [c] $\overline{M}_n = 635$, bp in C_6H_6. ^1H NMR in $CDCl_3$ with Me_4Si reference: δ 1.3–2.4 (m, CH_2, 32), 4.5 (broad s, $HCNO_2$, 2), 11.6 (s, COOH, 2). Reference mixture, 1:1 mole ratio dodecanoic acid + 1-nitrododecane: δ 1.3–2.4 (m, CH_2, 44), 4.39 (t, CH_2NO_2, 2), 11.5 (s, COOH, 1). [d] $\overline{M}_n = 780$, bp in C_6H_6. ^1H NMR: δ 1.3–2.4 (m, CH_2, 34), 4.5 (s, $HCNO_2$, 2), 11.4 (s, COOH, 2). [e] $\overline{M}_n = 780$, bp in C_6H_6. ^1H NMR: δ 1.3–2.4 (m, CH_2, 36), 4.5 (s, $HCNO_2$, 2), 11.2 (s, COOH, 2). [f] $\overline{M}_n = 750$, bp in C_6H_6. ^1H NMR: δ 1.3–2.4 (m, CH_2, 40), 4.5 (s, $HCNO_2$, 2), 11.3 (s, COOH, 2); also δ 5.05 (s, vinyl CH, trace). ^{13}C NMR: δ 180.48, 180.09, 179.70, 179.11, 178.07 (*C*OO), 123.03, 120.10 (vinyl *C*), 88.91, 88.71, 88.52, 88.26 (*C*NO_2), 34.05–20.86 (*C*H_2).

products and the procedures used. The first notable feature is the spread of number average molecular weights ($\overline{M}_n$) which, by GPC, vary from 1300 for preparation 2 to 4100 for preparation 5. In these two extremes, the main determinant of the molecular weight difference is undoubtedly the state of subdivision of the starting material. The effect of this parameter is more clearly shown in preparations 10 and 11 in which the other factors, time, temperature, and stirring mode, were constant; the $\overline{M}_n$ of the product from pellets was 2800 whereas that from the finely divided, recrystallized material[15] was 1800, and yet the yields were essentially equivalent. A similar order of change was shown in the work of Keller et al.[9b] They observed peak molecular weights by GPC of 1240–1360 for products from recrystallized polyethylene and 1750–1860 for that from bulk pellets.[17] Ballard and Dawkin working with recrystallized starting material obtained product $\overline{M}_n$'s of 1200–1550 by osmometry and viscometry. In neither of these cases were polydispersity indexes given although calculations in this laboratory[19] from the data of Keller et al. suggest that their products had polydispersity indexes of about the same order as ours.

The effect of agitation is dramatically illustrated by comparing preparations 7 and 12 where all factors are the same except for the method of stirring. In a magnetically stirred mixture, the bed of pellets floats on the more dense acid and rotates very slowly as a relatively undisturbed mass. Mechanical paddle stirring constantly tumbles the pellets as the bed rotates at a rate very close to that of the stirrer rate. The yield of solid from the magnetically stirred reaction was 91% and the $\overline{M}_n$ (GPC) was 2600. The mechanically stirred mixture product had a much lower $\overline{M}_n$ (1900) and the yield of solid was only 33%; however, it was accompanied by a substantial amount of low molecular weight grease. We shall discuss these greases later. A similar agitation effect is shown in the results of preparations 5 and 6.

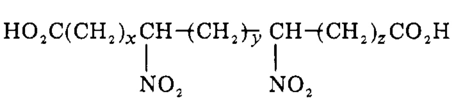
As far as acid concentration effects are concerned, other things being equal, there seems to be relatively little difference between the two kinds of fuming acid (preparations 3 and 7 or 4 and 14). But the more aqueous concentrated nitric acid is considerably more destructive (preparations 16 and 17).

Polydispersity indexes ($\overline{M}_w/\overline{M}_n$) for the products listed in Table I vary between about 1.05 and 1.3, but there is no apparent relationship between the breadth of dispersity and the preparation conditions. The remarkable feature is that regardless of conditions, the indexes are so very near unity or monodispersity. This in turn must reflect the integrity of the crystallites in the starting polymer. In most of the examples, yields of high molecular weight products were high (90–95%) which would be expected from the high crystallinity of the original polyethylene or, conversely, the low amorphous content.

The matter of nitration will now be considered. As seen in Table I, our products in general show a much higher degree of nitration than those of Keller and co-workers who reported carboxyl to nitro group ratios of about 11:1.[8,9,20,21] Thus, preparation 17 with a $COOH/NO_2$ ratio of 1.63 is very extensively nitrated. However, most of our examples cluster around 3 or 4:1. A more pictorial way of expressing these ratios is in terms of percentage nitration.[22] For example, a $COOH/NO_2$ ratio of 4:1 corresponds to 50% nitration which is to say that statistically, 50% of the molecules are mononitrated and the remainder are free of nitro groups. A ratio of 1.63 (preparation 17, Table I) corresponds to about 125% nitration; that is, statistically 75% of all molecules are mononitrated and the remainder are dinitrated. There may, of course, be distributions among unnitrated and other polynitrated species, but there is presently no way of distinguishing such detail.

The Nitro Carboxylic Greases. The major difficulty in fully characterizing the high molecular weight acids is their relative intractability and the fact that the functional groups are so highly diluted by the hydrocarbon residue. But in several experiments in Table I, the solids were accompanied by acetone-soluble greases (preparations 6, 12, 13, and 17). We consider these to be low molecular weight homologues of the solids and present them as tractable models whose characterization could reinforce otherwise questionable conclusions about the solids.

In Table II are summarized the data on characterization of these greases. The methods include elemental analyses, infrared spectra, ^1H and ^{13}C NMR, nonaqueous titration, ebullioscopic molecular weights, and additional data on several derivatives. In appearance they are light-yellow, opalescent materials with the consistency of honey, and all have very similar compositions regardless of differences in the preparation conditions. In summary, they have compositions corresponding to 4, where $x + z \simeq 0$–6 and $x + y + z \simeq 14$–17.



$$HO_2C(CH_2)_xCH\underset{NO_2}{|}\!-\!(CH_2)_y\!-\!CH\underset{NO_2}{|}\!-\!(CH_2)_zCO_2H$$

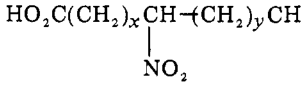
4

Again, it must be understood that this is a statistical composition leaving open the possibility that some species are less highly nitrated and others more highly nitrated.

The infrared spectra clearly show almost exactly a 1:1 mole ratio of carboxyl to nitro groups and elemental analyses indicate compositions corresponding to about $C_{10}H_{19}NO_4$ or a multiple thereof. The simple formulation could correspond to either **5** or **6**. Structure **6** can be discarded out of hand be-

$HO_2C(CH_2)_8CH_2NO_2$

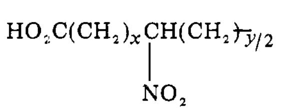
5



$HO_2C(CH_2)_x\underset{NO_2}{CH}(CH_2)_yCH_3$

6, $x + y = 7$

cause the survival of terminal methyl groups would be vanishingly small. Structure **5** with the terminal primary nitro group is ruled out because the proton NMR spectra show that the carboxyl proton (δ 11.3–11.5) and protons α to the nitro group (δ 4.5) are present in a ratio of 1:1 not 1:2; the 1:2 ratio is clearly seen in an equimolar reference mixture of dodecanoic acid and nitrododecane. Therefore, the structure must be a dimer of a fragment such as **7**.



$HO_2C(CH_2)_x\underset{NO_2}{CH}(CH_2)_{y/2}$

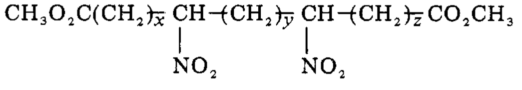
7

The mass spectrum of preparation 3, Table II, shows a major parent ion with mass number 398 which would correspond approximately to **4** with $x + y + z = 14$, and potentiometric titration clearly distinguished two carboxyl groups at breaks corresponding to the molecular weight (399) and the neutral equivalent (199).[23] Thus, the titration data agree almost exactly with the mass spectral data.

From the ^{13}C NMR, we conclude that the nitro groups are near neighbors of the carboxyl groups. The ^{13}C resonances of the COOH and C–NO2 groups are each resolved into several peaks. These different chemical shifts can be evident only if the two groups are within a few carbon atoms distance of one another, otherwise the resonances would appear as two single peaks with chemical shifts somewhat lower than the minor peaks observed for each. The nitro groups must, therefore, be in positions α, β, γ, and perhaps δ with respect to the carboxyls and hence the conclusion that in **4** $x + z \simeq 0–6$.

These low molecular weight materials show a very strong tendency to associate as reflected in the inordinately high molecular weights determined ebullioscopically in benzene.

The values shown in Table II (650–750) were, in fact, obtained by extrapolating to zero concentration. Nitroalkanes are known to associate more or less strongly, depending on the solvent;[24] the presence of a multiplicity of nitro groups and strongly associating carboxyl groups in the same molecule no doubt accounts for the high apparent molecular weights. Esterification of preparation 3 gave a dimethyl ester whose integrated proton NMR and elemental composition conformed closely to the C_{23} product **8**. The ebullioscopic molecular



$CH_3O_2C(CH_2)_x\underset{NO_2}{CH}(CH_2)_y\underset{NO_2}{CH}(CH_2)_zCO_2CH_3$

8, $x + y + z = 17$

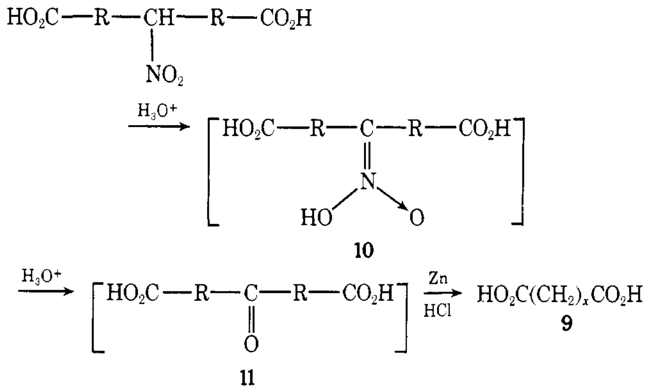
weight of the ester was 470 (theory 474) with no indication of association.

Final support in characterizing the nitro-carboxylic greases was found in the Clemmensen reduction of preparation 4 to a semicrystalline dicarboxylic acid whose composition, integrated proton NMR, molecular weight, infrared, and neutral equivalent showed an average composition corresponding to **9**. It was presumably formed by an acid-catalyzed Nef reaction

$HO_2C(CH_2)_{17}CO_2H$

9

and sequential Clemmensen reduction of the derived ketone group(s); schematically



10

11

9

The yield of **9** was very low (<2%) presumably because of poor solubility relationships in the Clemmensen reduction system and because the simple aqueous acid catalyzed Nef reaction of a free nitro compound is extremely slow; ordinarily the Nef reaction is carried out on an alkali metal salt of the already enolized nitronic acid (cf. **10**) from which the ketone is generated very rapidly.[25]

To the extent one believes the greases to be models of the long-chain acids, the implication is that the nitro groups in those acids are very near the carboxyl ends. It follows that the nitration reaction is not random. This near-terminal nitro group disposition may simply be determined by the accessibility of the polar-ended crystallites to the nitrating species. That is to say, after oxidation of crystallite chain folds, the residual crystallites would have polar surfaces (COOH) at the longitudinal termini. One could conceive that the nitrating species would penetrate at least a short distance into such surfaces.

Nitro Group Removal. Earlier we referred to the ambiguity of published conclusions concerning the nitro groups in the high molecular weight acids.[6,8,9a,10] We now introduce evidence which shows conclusively that the nitro groups are not primary but secondary and that their removal by hot sulfuric acid generates ketonic carbonyls not carboxyl groups.

Procedures in the literature involve heating the nitro acids with concentrated sulfuric acid in sealed tubes for periods of about 1 to 2 days.[26] We found this unnecessarily cumbersome and instead achieved the same result by stirring recrystallized nitro acid with 95–97% sulfuric acid in an open glass vessel at 85–95 °C for 6 h. This eliminates substantially all the nitro groups as judged by infrared spectra. As obtained, these products are dark gray and dissolve in boiling xylene to form dark gray-brown solutions. This color obscures the phenolphthalein end point in neutral equivalent determinations so the products must be bleached. Treatment with 15% hydrogen peroxide at 60–70 °C served this purpose.[27]

The data on these "denitro" acids are summarized in Table III. The salient point is that, considering the nitro group contents of the precursor acids, the neutral equivalents of the denitrated products should be between 15 and 25% lower *if the nitro groups are converted to carboxyls,* but such is not so. In general, the neutral equivalents were within experimental error (±2–5%) of being identical for product and precursor, and where there is a significant difference, the deviation is toward larger neutral equivalents. Thus, the nitro groups are not converted to titratable end groups. The only alternative is that they are secondary at the outset, and the sulfuric acid converts them to ketonic carbonyls via the Nef reaction (see above). This should augment the carbonyl infrared absorption band relative to an internal standard such as a CH band. Unfortunately, this could not be established by infrared peak heights because absorption by the putative keto carbonyls is not linearly additive to that of the carboxyl car-

Table III
Keto Acids Derived from the Nitro Acids

Keto acid prepn No.[a]	Nitro acid Table I prepn No	GPC data $\overline{M}_w$	GPC data $\overline{M}_n$	GPC data PI[b]	$\overline{M}_n$ by titration	Sulfuric acid treatment time, h
1	4	4500	3200	1.26	2450	6
2	4	4300	3200	1.20	2500	4
3[c]	7	3790	2900	1.16	2150	3
4	8	3200	2500	1.13		25
5	8	3000	2500	1.11	2500	25
6	9	2800	2300	1.08	2150	6
7	13	3600	3000	1.20		6
8	14 F	3400	2600	1.28	2000	5
9	17	2900	2500	1.17		6

[a] Bleached with H_2O_2 unless otherwise noted. CO_2H/NO_2 IR ratios varied between about 15:1 and 30:1, NO_2 absorbance being so weak as to be near the noise level. [c] Bleached with Cl_2 in water. Product contained organic chlorine. [b] Corrected for instrumental broadening.

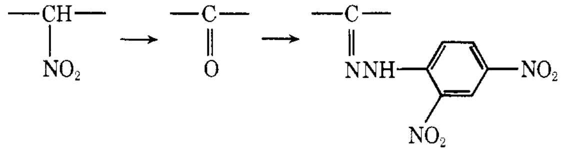
Table IV
Infrared Absorption Ratios[a] of Nitro Acids and DNP's[b] of Keto and Reduced Keto Acids

Exptl No.	Nitro acid Table I prepn No.	NO_2/CO_2H ratio[c]	Keto acid Table III prepn No.	Hydrazone/CO_2H ratio[d] Before reduction	Hydrazone/CO_2H ratio[d] After reduction	% reduction
1	17	0.61	9	0.78	0.41[e]	47
					0.27[f]	65
2	13	0.39	7	0.76	0.24[f]	68
3	6	0.38	g	0.71	0.35[h]	51
					0.19[i]	73
4	9	0.27	6	0.43	0.30[j]	30
					0.22[k]	49
5	4	0.21	2	0.45	0.18[h]	60
					0.13[j]	71

[a] 2% in KBr wafers. [b] 2,4-Dinitrophenylhydrazone. [c] 1550/1710 cm^{-1} absorbance ratio. [d] 1615/1710 cm^{-1} absorbance ratio. [e] 72-h Clemmensen, atmospheric pressure. [f] Wolff–Kishner. [g] Prepared but not further characterized. [h] 24-h Clemmensen, atmospheric pressure. [i] 96-h Clemmensen, atmospheric pressure. [j] 24-h Clemmensen, 145 °C, bomb. [k] 36-h Clemmensen, 145 °C, bomb.

bonyls at the wavelength of maximum absorption. There was some broadening of the carbonyl band but the evidence was at best only suggestive.

However, condensation of the "denitro" products with 2,4-dinitrophenylhydrazine gave hydrazones whose infrared spectra showed strong, well-resolved bands at 1615 and 1590 cm^{-1}. Moreover, the peak height ratios of the 1710 (carboxyl carbonyl) to 1615 hydrazone bands were approximately proportional to the CO/NO_2 ratio in the parent nitro acids thus demonstrating the transformations



and establishing that the "denitro" acids are in fact keto acids. Representative infrared data are compiled in Table IV.

Reduction of the Keto Acids. The keto groups in the keto acid can be partially reduced to methylene groups either by Clemmensen reduction with amalgamated zinc and hydrochloric acid or by Wolff–Kishner reduction with hydrazine and potassium *tert*-butoxide.

In the Martin modification of the Clemmensen reduction,[28] a water-insoluble organic phase is used to dissolve the substrate. We used xylene. However, when the reaction is run at atmospheric pressure, the maximum temperature attainable is limited by the reflux temperature of the aqueous hydrochloric acid (~105 °C). This is not high enough to dissolve the keto acid. Thus, one is dealing with a four-phase system: the dispersed keto acid, the organic liquid, the aqueous acid, and the insoluble zinc. Under these conditions, reduction is very slow so that even after 96 h of reaction time it was only about 75% complete as inferred from the infrared spectrum of the derived 2,4-dinitrophenylhydrazone.

When the reaction is carried out in a closed bomb at 145 °C, the keto acid is completely soluble in the xylene, but even under these conditions complete reduction was not achieved even after 36 h.

Modified Wolf–Kishner reduction[29] of the keto polymers in refluxing xylene with hydrazine and potassium *tert*-butoxide also eliminated a substantial proportion of the keto groups. In this case, the reaction should ostensibly be homogeneous since the keto acids are soluble in boiling xylene. However, the potassium *tert*-butoxide converts them to potassium salts which are insoluble gels. Thus, the reaction remains heterogeneous and consequently very slow, being about 65–70% complete in 18 h.

The infrared data relating to these experiments are given in Table IV.

Experimental Section

Materials and Methods. The polyethylene resin used was high-density Alathon 7040,[12] except one instance in which Alathon 7050 polyethylene resin was used.[13] This is noted in Table I.

The nitric acids were commercial concentrated,[30] 90% fuming,[30] or red fuming.[31]

Titration of the high molecular weight products was conducted as follows: the titrant was prepared by dissolving 1.4 g of KOH in 70 mL of ethanol and then diluting with 375 mL of reagent-grade xylene. The titrant is nominally 0.5 N and was standardized against decanoic acid (0.2 g) in 25 mL of methanol with 3 drops of 5% methanolic phenolphthalein as indicator. To titrate the oxidation products, 1 g was dissolved in 50 mL of xylene heated just below its boiling point (~125 °C) on a magnetic stirring hotplate and 3 drops of phenolphthalein was added. The stirred solution was kept hot and titrated dropwise to the pink end point. When stearic acid was run as a control, neutral equivalents within ±0.5% of the theoretical value were obtained.

Infrared spectra were run on a Perkin-Elmer Model 621 grating spectrophotometer.

^{1}H NMR spectra were run on a Varian A-60 spectrometer and ^{13}C spectra on a Bruker WH-90 (22.63 MHz) spectrometer.

Gel-permeation chromatography (GPC) was carried out on 0.125% solutions in 1,2,4-trichlorobenzene through three linear styragel columns at 150 °C using National Bureau of Standards 1475 polyethylene for calibration. In this way, weight average molecular weights ($\overline{M}_w$) and number average molecular weights ($\overline{M}_n$) were obtained and from them the polydispersity indexes (PI = $\overline{M}_w/\overline{M}_n$).

General Oxidation Procedures. Two setups were used which differed mainly in the method of stirring, i.e., either with magnetic stirring or mechanical paddle stirring.

For magnetic stirring, a 2-L three-neck flask was fitted with an Allihn condenser (30-cm jacket) whose upper outlet was vented into a cascading water trap by means of an adapter and Tygon tubing. The flask was then equipped with an electric heating mantle and a magnetic stirrer (1.5-in. bar coated with Teflon fluorocarbon resin). The two remaining necks were glass stoppered, one being used for intromission of a thermometer if necessary.

For mechanical stirring, a similar setup was used but the center neck was equipped with an all-glass stirrer bearing a rod with a 10-cm paddle of Teflon fluorocarbon resin. The rod was attached to an electric motor adjusted to rotate the stirrer at a rate of 140–150 rpm.

The flask was charged with 900 mL of the appropriate acid and 200 g of polyethylene pellets, then stirring and heating were begun.

When concentrated nitric acid (71%) was used, the mantle temperature was set to give a reaction mixture temperature of 110–115 °C. After about 15 min, brown fumes were evolved and refluxing began. The original mantle setting was maintained throughout the whole reaction time. With 90% fuming nitric acid, reflux began at a nominal mixture temperature of 50–60 °C and the mantle setting required to achieve this was left constant. After about 24 h, the pot temperature had risen to 80–90 °C and refluxing continued. Red fuming nitric acid behaved very much like the 90% fuming acid.

After the appropriate reaction time, the mixture was cooled to room temperature and poured into 2 L of crushed ice and was stirred occasionally until the ice melted.

When short reaction times and/or magnetic stirring were used, the product was a mixture of dispersed fines and apparently intact pellets. These were separated by passing the aqueous suspension through a 14-mesh (ASTM) stainless-steel screen and the pellets were washed free of fines by agitating the pellets on the screen while washing with water. The fines and pellets were kept separate. The easily friable pellets were dispersed with water in a high-speed blender and thenceforth the fines and dispersed pellets were treated similarly. In some reactions the product was completely dispersed so the separation was not necessary.

The suspended solid was collected on a coarse frit funnel and redispersed in 2 L of water which was then heated to the boiling point and filtered again. This was repeated several times until the filtrate was neutral. The solid on the frit was sucked free of adherent water and was dried to constant weight in a vacuum desiccator over phosphorus pentoxide. Filtrates up to this point were discarded.

The dried solid was boiled with three 1-L portions of acetone, the filtrates being combined and reserved for separate workup.

The solid was sucked dry and recrystallized from xylene (20 mL/g). It was then collected, washed with hexane, and dried to constant weight in a vacuum oven at 95 °C (overnight) before titrating or otherwise manipulating.

The acetone filtrate was freed of bulk solvent on a rotary evaporator and if any residual low molecular weight material remained, it was further freed of solvent by heating at 80–90 °C while pumping at 0.1–0.3 Torr.

Nitro Group Removal and Bleaching. A solution of 10 mL of water and 500 mL of concentrated sulfuric acid in a 1-L Erlenmeyer flask was heated to 80–85 °C while being stirred on a magnetic stirrer hotplate. Fifty grams of finely divided, recrystallized nitroalkanoic acid was added in teaspoon portions allowing each to disperse before adding the next. When all was added, stirring and heating were continued for 6 h. The gray-black mixture was then cooled to room temperature and poured into 2 L of crushed ice. The product was collected and washed by dispersing in several portions of boiling water as described above. When the wash was neutral, the product was sucked free of the bulk of water and was redispersed in 500 mL of water. To it was added 100 mL of 30% hydrogen peroxide and the slurry was stirred and heated at 65–70 °C for 6 h. It is important not to overheat the mixture because vigorous foaming may occur and eject material from the flask.

The product was then collected on a coarse frit funnel and washed as before until free of peroxide (negative test with starch-KI paper). It was then washed with 1 L of acetone in portions, sucked dry, and dried in a vacuum oven at 95–100 °C. The dry product was recrystallized from xylene (20 mL/g) as previously described. Recovery was essentially quantitative except for minor mechanical losses.

Clemmensen Reduction at Atmospheric Pressure. One hundred grams of mossy zinc was amalgamated with 10 g of mercuric chloride, 150 mL of water, and 5 mL of concentrated hydrochloric acid by shaking for 5 min. The liquid was decanted and the zinc was washed by decantation with two 100-mL portions of water.

The zinc, together with 75 mL of water, 175 mL of concentrated hydrochloric acid, 150 mL of xylene, and 5 g of keto acid was added to a 1-L, three-neck flask equipped with a mechanical stirrer and an efficient reflux condenser. The mixture was vigorously stirred and heated at reflux temperature for 24 h and then cooled to room temperature. It was diluted with 500 mL of water and the polymer–solvent slurry was decanted from the zinc residue. Any product adhering to the zinc was dissolved by boiling briefly with 50 mL of xylene and the hot xylene was decanted into the initial decantate which was then cooled to room temperature. The product was collected on a coarse frit funnel and washed with 1 L of acetone, sucked dry, and dried further in a vacuum oven at 95–100 °C. It was dissolved in 200 mL of boiling xylene and the hot solution was suction filtered through a preheated medium frit funnel to remove traces of zinc. The filtrate was cooled to room temperature and the solid was collected, washed with hexane, and again dried in a vacuum oven. About 3.5–4 g of material was recovered.

Clemmensen Reduction under Pressure. The ingredients described above were added to a 1-L, glassed lined bomb and the bomb was sealed. It was then shaken and heated at 145 °C for 24 h. After cooling, the mixture was worked up as described above.

Wolff–Kishner Reduction. A mixture of 5 g of keto acid, 5 g of potassium *tert*-butoxide, 5 mL of anhydrous hydrazine, and 250 mL of xylene was boiled under reflux in a nitrogen atmosphere for 18 h. The mixture was cooled to room temperature and the product was collected on a coarse frit funnel. It was then washed with 500 mL of ethanol in portions and sucked dry. It was suspended in a mixture of 250 mL of xylene and 50 mL of 12 N sulfuric acid which was then magnetically stirred and boiled gently for 15 min. After cooling, the product was again collected, washed with 500 mL of acetone in portions, sucked dry, and boiled with several 200-mL portions of water until the wash was neutral. After washing with acetone again and drying, it was recrystallized from xylene as previously described.

2,4-Dinitrophenylhydrazone Formation. A mixture of 25 mL of xylene, 0.5 g of keto acid or reduced keto acid, and 0.1 g of 2,4-dinitrophenylhydrazine was boiled under reflux for 2 h and cooled to room temperature. The product was collected and washed on the funnel with acetone. The solid was suspended in 50 mL of acetone, the mixture was boiled gently on a steam bath for 5 min, and the product was collected again and sucked dry.

Clemmensen Reduction of Nitro Carboxylic Grease. A 5-g portion of the nitro carboxylic grease from preparation 6, Table I, was subjected to Clemmensen reduction at atmospheric pressure for 18 h as described above for the high molecular weight products. The xylene layer was separated, washed with two 100-mL portions of water, and then dried over anhydrous magnesium sulfate. The xylene was distilled out under vacuum at 80–90 °C and the residual oil was freed of solvent by pumping at 0.1–0.3 Torr while heating on a steam bath. The crude wax was boiled with 100 mL of hexane for 10 min then chilled briefly in ice to solidify the oil. The supernatant hexane was quickly poured off and chilled thoroughly to obtain 0.1 g of white solid, mp 73–77 °C. Neutral equivalent found 150; mol wt (freezing point in benzene) 325; NMR ($CDCl_3$) δ 1.28 (s, CH_2, 15), 2.34 (t, J = 6 Hz, α-CH_2, 2), 10.9 (s, COOH, 1). The data correspond approximately to the dicarboxylic acid $HO_2C(CH_2)_{17}CO_2H$, mol wt calcd 328.5.

Esterification of Nitro-Carboxylic Grease. A mixture of 8 g of the grease from preparation 17, Table I, 100 mL of toluene, 10 mL of methanol, and 0.5 g of p-toluenesulfonic acid was refluxed under a Dean-Stark head for 5 h. The solution was cooled and extracted with two 50-mL portions of saturated sodium bicarbonate and two 50-mL portions of water. The organic layer was dried over anhydrous magnesium sulfate and freed of solvent by vacuum distillation on a steam bath. Residual solvent was removed by pumping at 0.1–0.3 Torr while heating at 85–90 °C. Anal. Calcd for $C_{23}H_{42}N_2O_8$: C, 58.2; H, 8.9; N, 5.9; mol wt, 474.6. Found: C, 58.0; H, 9.1; N, 5.4; mol wt (bp in benzene), 470.

The infrared spectrum showed a characteristic ester band at 1735 cm^{-1} and additional bands at 1190, 1160, 1100, 1010, and 850 cm^{-1} all absent in the staring material: NMR ($CDCl_3$) δ 1.29 (s, CH_2), 2.32 (t, J = 6 Hz, α-CH_2), 3.69 (s, OCH_3), 4.50 (s, $HCNO_2$), and no COOH absorption at δ 10–11.

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(11) These preliminary experiments were done by Dr. R. C. Ferguson of this laboratory.
(12) The polymers were commercial resins in the form of extruded pellets about 4 mm × 7 mm in size. They were obtained from the Plastic Products and Resins Department, E. I. du Pont de Nemours and Co., Wilmington, Delaware. Alathon polyethylene resin is a registered trademark of the Du Pont Co. Alathon 7040 polyethylene resin has $\overline{M}_w$ = 89 000, $\overline{M}_n$ = 25 000 (by GPC).
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(15) Pellets were recrystallized from xylene (50 mL/g) without any special care to control cooling rate or optimize crystal growth. Boiling solutions were merely allowed to cool spontaneously to room termperature.
(16) Corrected for instrument broadening.
(17) Marlex 6009.
(18) Rigidex 2.
(19) Private communication from Mr. C. R. Ginnard of this laboratory.
(20) For our estimations, we used the value 1.00 for the ratio of the extinction coefficient of one COOH group to one NO_2 group. For known mixtures of decanoic acid and 1-nitrododecane, the ratio varied between 0.82 and 1.22 depending on whether the samples were run neat or in solution in dichloromethane or mineral oil. The average was 1.03 which for practical purposes we took to be unity. There is further uncertainty in this, however, because although the ratio was linear with different proportions run neat, they were significantly nonlinear in solution. Keller and Udagawa (ref 8) used the ratio 0.71.
(21) Nitrogen elemental analyses are not useful in determining the degree of nitration because the low levels dealt with are within the error limit of combustion analysis.
(22) Percent nitration can be calculated from the relationship 200/($COOH/NO_2$ ratio) assuming only that there are two carboxyl groups per molecule.
(23) The solvent was acetone and the titrant was tetra(*n*-butyl)ammonium hydroxide. I thank Mr. Robert J. Berndt for the measurements.
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(26) In the procedure of ref 10, 0.3 g of nitro acid was heated with concentrated sulfuric acid in a sealed tube at 70 °C for 20 h. In ref 9a, the treatment was with 0.2 g at 60 °C for 2 days.
(27) Keller and Udagawa (ref 9a) used activated charcoal in hot xylene solutions, but this failed in our hands. Ballard and Dawkins (ref 10) used hot concentrated nitric acid but in at least one such trial we had evidence for the reintroduction of nitro groups.
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An ESR Study of Oxidation in Uniaxially Deformed Polybutadiene and Polyisoprene

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ABSTRACT: The possible reactions of polybutadiene and other diene rubbers, with oxygen during initial processing, low-temperature mechanical degradation, and subsequent handling, are reviewed. Radicals formed following tensile testing of polybutadiene and polyisoprene at 83 K in predominantly nitrogen atmospheres, but containing different amounts of oxygen, are examined using electron spin resonance (ESR) techniques. It is concluded that two or more radical species result from mechanical deformation at low temperature when oxygen is present. Radicals identifed are a peroxy radical and most probably an allyl radical arising from main chain rupture. Peroxy radicals are shown to arise mainly from combination of radical species with oxygen in the test environment, although a small proportion is attributed to oxygen incorporated into the rubber network during processing. The relative stability with increasing temperature of the peroxy to other radical species present is studied quantitatively.

I. Introduction

The effect of atmospheric oxygen on unsaturated rubbers at ambient temperature and above is pronounced and has been widely studied.[1,2] It is known that chain rupture mechanically induced by mastication produces radicals which are stabilized by reaction with oxygen.[3] For natural rubber this leads to a reduction in molecular weight into the processable range. More recently, the application of electron spin resonance (ESR) technique to monitor radical formation during mechanical deformation of diene rubbers in the glassy state, close to the liquefaction temperature of nitrogen, has also revealed oxygen-containing radicals.[4–8] The reactivity of oxygen with polymer radicals formed by mechanical degradation has been recently reviewed by Sohma and Sakaguchi,[9,10] while DeVries[11] has reviewed radical formation in rubbers. The presence of such oxygen-containing radicals is

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