Determination of the Purity of 2, 2-Diphenyl-1-picrylhydrazyl and 2, 2-Di-(*p*-tolyl)-1-picrylhydrazyl by Iodometry

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2, 2-Diphenyl-1-picrylhydrazyl (DPPH) has been often employed as a radical scavenger and as a standard substance for ESR measurements. In each case the purity of the hydrazyl free radicals was assumed to be 100% and a satisfactory method of determining the purity was not established.

Elemental analysis may be a measure of purity, but it is a rather insensitive way to determine the purity. It has been reported that DPPH reacts quantitatively with hydroquinone to yield 1, 1-diphenyl-2-picrylhydrazine and benzoquinone,[1] but no experimental results were presented. The extent of conversion of various hydrazines to the corresponding hydrazyl free radicals, has been estimated by the reaction of the hydrazyl free radicals with ascorbic acid.[2]

1) S. Goldschmidt and K. Renn, *Ber.*, 55, 628 (1922).
2) D. Braun, I. Löflund and H. Fischer, *J. Polymer Sci.*, 58, 667 (1962).

TABLE I. IODOMETRIC TITRATION OF DPPH AND DTPH

Sample	Weight	1/100 N $Na_2S_2O_3$ (f=0.9908) calcd. volume* ml.	Volume consumed ml.	$\frac{\text{Volume consumed}}{\text{Calcd. volume}} \times 100$	
Crude DPPH before recrystallization	37.7	10.02	8.67	86.3	Average 87.1
	24.1	6.39	5.56	87.1	
	29.5	7.51	6.60	87.8	
DPPH after once recrystallization	28.7	7.35	7.11	96.8	97.0
	28.3	7.23	7.03	97.1	
DTPH freshly prepared in benzene**	60.36	14.42	14.17	98.3	98.6
	60.36	14.42	14.24	98.8	

* Based on one equivalent for reduction of the hydrazyl free radicals.
** The concentration of DTPH was calculated from the weight of the hydrazine used in its preparation.

The authors have found that DPPH and analogous hydrazyl free radicals can be satisfactorily determined by iodometry. The technique is almost the same as that used in the determination of organic peroxides.[3]

The iodometric determination of relatively stable phenoxy radicals has been reported by Müller and Ley.[4] They reduced the phenoxy radical to the corresponding phenol with sodium iodide using glacial acetic acid as a solvent and carrying out the determination under an atmosphere of carbon dioxide.

DPPH, prepared by the method of Goldschmidt and Renn,[1] was recrystallized from benzene-ligroin, then dried under reduced pressure at 77°C for 50 hr.

Found: C, 54.7; H, 3.08; N, 18.0. Calcd. for $C_{18}H_{12}O_6N_5$: C, 54.8, H, 3.07; N, 17.8%.

1, 1-Di-(*p*-tolyl)-2-picrylhydrazine was prepared by the method of Poirier and Benington.[5] M. p. 159.0°C (uncorrected), lit. 161°C.[5]

Found: C, 56.4; H, 4.16; N, 16.3. Calcd. for $C_{20}H_{17}O_6N_5$: C, 56.7; H, 4.05; N, 16.5%.

The hydrazine was oxidized to 2, 2-di-(*p*-tolyl)-1-picrylhydrazyl (DTPH) with a freshly prepared suspension of lead dioxide in benzene. DTPH is as stable as DPPH in solution. However, an attempt to separate pure DTPH in solid form failed. Gradual evaporation of a concentrated solution of DTPH in benzene under reduced pressure gave a dark violet solid which turned brown on standing. The solid DTPH reported in the literature[6] also seems to be contaminated since its analytical data do not agree with the calculated values, and N–H absorption occurs in its infrared spectra.

All other reagents were commercial materials.

Ten milliliters of redistilled acetic anhydride and an excess of sodium iodide (ca. 1 g. of sodium iodide for 0.1 g. of hydrazyl) were added to the hydrazyl in a glass stoppered flask. After being allowed to stand in the dark for 10 min., 50 ml. of water and 15 ml. of benzene were poured into the flask; the mixture was then saturated with sodium sulfate to clear the aqueous layer. The liberated iodine was titrated with 1/100 N sodium thiosulfate solution with vigorous shaking and using 0.5% starch solution as an indicator. Benzene was added to take up colored organic products so that the end point of titration was clearly detectable.

The results are shown in Table I.

The products from the titration were studied spectrophotometrically. The spectrum of DPPH after reduction with sodium iodide was exactly the same as that of 1, 1-diphenyl-2-picrylhydrazine, showing a maximum absorption at 320 mμ. The DPPH which had been formed in the reduction and extracted into benzene, was quantitatively reoxidized to DPPH on treatment with lead dioxide.

The origin of the hydrogen transferred to the hydrazyls is not clear. The violet color of the hydrazyl was observed to disappear after addition of sodium iodide to the acetic anhydride solution of the hydrazyl. This indicates that the reduction of the hydrazyl is completed in acetic anhydride before addition of water. Small amounts of acetic acid in the acetic anhydride may be the source of the proton transferred to the hydrazyl. Under the present experimental conditions, less than 0.1% of acetic acid in the acetic anhydride would be sufficient to complete the reaction. Reduction of the hydrazyl by sodium iodide also proceeds rapidly in acetic acid. However, the use of acetic acid as solvent brings about spontaneous oxidation of the sodium iodide unless the reaction is carried out under an

3) K. Nozaki, *Ind. Eng. Chem., Anal. Ed.*, **18**, 583 (1946).
4) E. Müller and K. Ley, *Chem. Ber.*, **87**, 922 (1954).
5) R. H. Poirier and F. Benington, *J. Org. Chem.*, **19**, 1157 (1954).
6) M. M. Chen, A. F. D'Adamo and R. I. Walter, ibid., **26**, 2721 (1961).

atmosphere of inert gas. The following reaction scheme may be proposed from these observations.

$$2\,\text{Hydrazyl} + 2\text{NaI} + 2\text{CH}_3\text{COOH} \rightarrow 2\,\text{Hydrazine} + 2\text{CH}_3\text{COONa} + \text{I}_2 \quad (1)$$

The ratio of the volume consumed to the calculated volume of 1/100 N sodium thiosulfate will then express the purity of the reducible nitrogen radicals in the sample. The purity of DPPH is quite high. Although DTPH is not a stable solid, conversion of the hydrazine to the hydrazyl is almost complete in solution.

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