THE EFFECT OF THE STRUCTURE OF TRI-SUBSTITUTED THIOUREAS ON EFFICIENCY AS DE-OZONIZERS*

A. M. Lipkin, L. K. Zolotarevskaya, A. Ye. Grinberg, Ya. A. Gurvich, L. G. Angert, S. D. Razumovskii and G. Ye. Zaikov

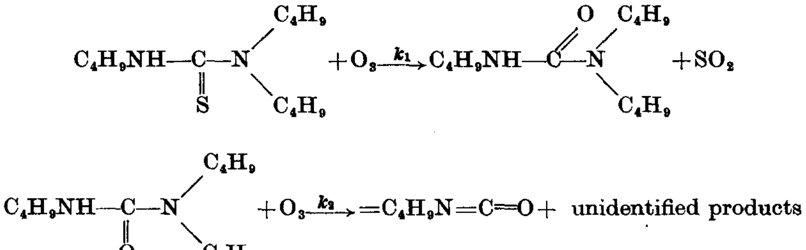
Institute of Chemical Physics, U.S.S.R. Academy of Sciences

(*Received* 6 *August* 1970)

The most efficient de-ozonizers (DO) such as *p*-phenylenediamine and quinoline derivatives and their products of oxidation are dark in colour and are therefore unsuitable for use in light and coloured vulcanizates [1]. In contrast to this class of compounds, thiourea (TU) derivatives do not alter the colour of light resins although they are somewhat less effective [2]. The mechanism of protective action has been insufficiently dealt with in the literature. Vatanabe [3] showed that the higher the rate of reaction of TU derivatives at constant rate of ozone passage, the more effectively they protect polyisoprene solutions from decomposition. Hence the author concludes that for resins prepared from diene rubbers those compounds which are characterized by higher reactivity to ozone will be the most effective.

However, the observations made are only indirect arguments in favour of the assumption expressed. Quantitative data obtained by us regarding the rate of interaction of ozone with 1,3,3-tributylthiourea (TBTU) and C=C-bonds in the polymer macromolecule have been given in earlier papers [4, 5].

It was shown that the interaction of TBTU with ozone takes place in two stages [4]:



Using competing reactions the rate constant of the first stage k_1 was determined and appeared to be higher than that of the reaction of diene polymers with ozone.

---

* Vysokomol. soyed. **A14**: No. 3, 680–685, 1972.

TABLE 1. PROPERTIES OF SYNTHETIC TRI-SUBSTITUTED THIOUREA AND RATE CONSTANTS OF REACTION WITH OZONE

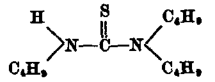
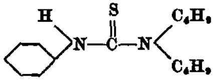
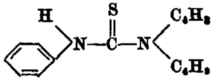
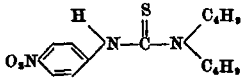
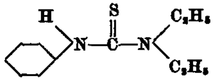
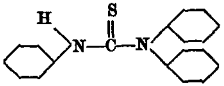
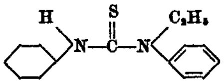
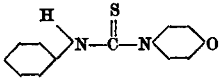
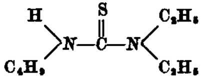
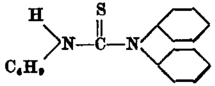
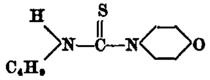
Compound, No	Conventional notation	Structural formula	Yield, %	M.p., °C	n_D^{20}	Molecular weight (ebullioscopic)		λ_{max}, mμ	Data of elementary analysis								k_1, l./mole·sec
									C		H		N		S		
						found	calc.		found	calc.	found	calc.	found	calc.	found	calc.	
1	TBTU		96	—	1·5158	240	244	246	65·08	64·3	11·46	11·1	12·47	13·1	10·75	11·5	1·7
2	DBHTU		61	23–24	—	261	270	246	67·04	66·7	10·85	11·10	9·74	10·3	12·06	11·89	1·4
3	DBPTU		82	82·3–83	—	257	264	248	68·30	68·3	8·94	9·04	11·0	10·6	11·9	12·1	1·3
4	DENPTU		78	85·5–86	—	315	309	242	60·22	59·30	7·57	7·44	14·01	13·72	10·33	10·31	1·0
5	DEHTU		85	119·5–120	—	217	214	244	61·77	61·60	10·36	10·30	12·98	13·10	14·94	14·90	1·6
6	THTU		58	98·5–99	—	326	328	250	71·0	70·6	10·53	10·53	8·88	8·59	8·51	8·70	1·4

TABLE 1. (*Cont.*)

Compound, No	Conventional notation	Structural formula	Yield, %	M.p., °C	n_D^{20}	Molecular weight (ebullioscopic)		λ_{max}, mμ	Data of elementary analysis								k_1, l./mole·sec.
									C		H		N		S		
						found	calc.		found	calc.	found	calc.	found	calc.	found	calc.	
7	EPHTU		70	54·2–55	—	258	262	243	68·6	68·8	8·64	8·40	10·9	10·7	11·8	12·2	0·9
8	MHTU		71	131–131·7	—	229	228	249	58·20	58·0	8·69	8·77	12·5	12·3	14·28	14·0	1·8
9	DEBTU		84	—	1·5343	184	188	244	57·12	57·3	10·36	10·61	14·22	14·8	16·0	17·0	1·5
10	DHBTU		52	86·8–87·6	—	303	296	249	69·0	68·9	10·87	10·9	9·10	9·44	11·10	10·82	1·4
11	MBTU		60	47·8–48·2	—	208	202	248	53·34	53·6	8·90	8·90	13·0	13·3	16·4	15·8	1·8

A study is made in this paper of the effect of the type of substituent on both nitrogen atoms on the rate of the reaction of TU derivatives with ozone and their efficiency as DO.

EXPERIMENTAL

Tri-substituted TU was prepared by interaction of corresponding isothiocyanates with secondary amines [6]. The characteristics of synthetic compounds and the rate constant of the reaction with ozone are shown in Table 1.

Compounds 1 and 9 in Table 1 are light yellow oily liquids which decompose on distillation, the remainder are crystalline substances purified by repeated recrystallization from alcohol to constant melting point. In the case of compounds 3, 5, 6 and 11, melting points coincide with literature data [3, 7–10] and the melting points of compounds 2, 4, 7, 10 have not been given in the literature.

The interaction of tri-substituted TU with ozone was examined by passing ozonized oxygen (ozone concentration $2\cdot3\times10^{-3}$ mole/l. or 5×10^{-2} vol. %) through a 0·2% solution in carbon tetrachloride of the compounds studied at room temperature. The error of measuring the rate constant of TU derivatives with ozone was 20%.

The behaviour of synthetic TU derivatives as colourless DO was examined in a vulcanizate prepared from natural rubber (NR) of a composition: pale crepe-100·0; stearin 1·0; thiuram 0·4; sulphur 2·0; magnesium oxide 3·5; zinc oxide 30·0; chalk 40·0 parts by weight.

Rubber mixtures were prepared in mills and vulcanized in a hydraulic press at 143°. The time elapsing before crack formation (τ, min) was taken as the criterion of ozone resistance of rubbers using samples exposed in an ozone compartment to an ozone concentration of $\sim1\cdot8\times10^{-4}$ vol. %. During testing the samples were subjected to static expansion ($\varepsilon=10\%$) or repeated deformation at a frequency of 12 cycles/min when $\varepsilon=20\%$.

The protective effect in rubbers was characterized by the ratio of time to crack formation in samples containing the compounds studied (τ_{DO}) to the same index for a control sample (τ_c).

RESULTS AND DISCUSSION

A study of the interaction of the compounds studied with ozone indicates that the stoichiometric reaction coefficient is two in every case. The liberation of sulphur dioxide during ozonization of tri-substituted TU indicates that the reaction first takes place as the C=S bond.

The rate constants (Table 1) derived by the method of competing reaction [4] exceed the rate constant of the reaction of ozone with C=C bonds of a NR macromolecule which is $7\cdot5\times10^5$ l./mole·sec [5]. The comparative remoteness of substituents on the nitrogen atoms of TU derivatives from the reaction centre (sulphur atom) accounts for the low induction effect of substituents. The type of this effect—the increase of the rate constant of the reaction with ozone during an intensification of electron-donor properties of the substituent (from $1\cdot0\times10^6$ to $1\cdot7\times10^6$ l./mole·sec on changing from *p*-nitrophenyl to alkyl in DBNPTU–TBTU compounds) may be easily explained in terms of the increase of reactivity of TU in relation to ozone with an increase in electron density on the sulphur atom.

Results of testing rubbers, which contain TU derivatives (Table 2) indicate that the type of substituent in TU has little effect on the physical and mechanical properties of rubbers, which are practically of equal value under optimum vulcanizing conditions. The effectiveness of these compounds as DO in rubber varies and depends on the chemical structure of substituents on the nitrogen atoms. Alkyl-substituted TU have the highest activity. The replacement of the alkyl radical in position 1 of TBTU by alicyclic, aromatic and *p*-nitro-aromatic radicals lowers the de-ozonizing effect until they disappear completely (e.g. on adding *p*-nitrophenyl). The same dependence is observed on changing the type of substituents in position 3.

TABLE 2. EFFECT OF TU DERIVATIVES ON THE MAIN PHYSICAL AND MECHANICAL CHARACTERISTICS AND DE-OZONIZING EFFECT OF VULCANIZATES PREPARED FROM NR

Compound, No.	Physical and mechanical properties of rubbers				Relative de-ozonizing effect in	
	modulus with 300% elongation, kg/cm^2	tensile strength, kg/cm^2	elongation, %			
			relative	residual	dynamic tests	static tests
Without DO	8	180	816	20	1·0	1·0
1	16	241	704	17	5·2	3·0
2	15	229	700	16	4·5	2·3
3	16	235	716	18	2·4	—
4	14	220	725	18	1·0	1·0
5	14	229	720	17	3·2	1·8
6	13	246	728	20	1·4	1·2
7	16	199	722	16	1·0	1·0
8	11	191	780	17	1·7	1·6
9	17	240	684	18	4·8	2·2
10	16	245	700	17	1·5	2·0
11	12	198	696	17	2·8	2·0

* Compound numbers correspond to the compound numbers in Table 1.

When examining the effectiveness of DO of several *p*-phenylenediamine derivatives with various substituents on the nitrogen atom we found [11] that there is a functional relation between the rate constant of the reaction with ozone k_{DO} and relative de-ozonizing effect of rubbers in the presence of DO τ_{DO}/τ_c

$$\log\frac{\tau_{DO}}{\tau_c}=A+B\frac{k_{DO}}{k_{ol}},$$

where k_{ol} is the rate constant of the reaction of ozone with model olefin (methyl oleate), A and B are coefficients which are constant for the entire series.

Figure 1 shows that among TU derivatives with different substituents in position 1 (curve *1*) an exponential dependence on k_{DO}/k_{ol} exists for $\log(\tau_{DO}/\tau_c)$. The same can be said with a certain degree of approximation about compounds with different substituents in position 3.

Figure 2 shows the dependence of the protective action of some TU derivatives on their concentration in rubber. With an increase in DO content the de-ozonizing effect of rubber increases in the case of effective DO (TBTU and DEBTU) and varies little or remains at the level of control rubber in the presence of THTU or DBNPTU, respectively. The order of effectiveness of these DO is retained.

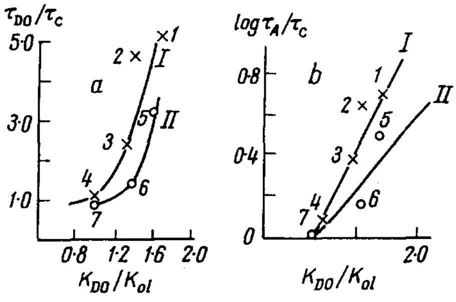


FIG. 1

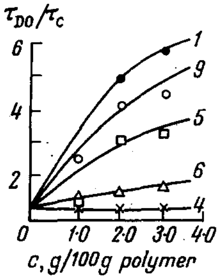


FIG. 2

FIG. 1. Dependence of τ_{DO}/τ_c (*a*) and log $\frac{\tau_{DO}}{\tau_c}$ (*b*) on $\left(\frac{k_{DO}}{k_{o1}}\right)$. Here and in Fig. 2 the numbers of points correspond to the numbers of compounds in Table 1.

FIG. 2. The effect of the concentration of tri-substituted TU in rubber on de-ozonizing effect under dynamic test conditions.

Data of Figures 1 and 2 prove that direct reaction with ozone has a significant role in the protective action of TU examined.

Attempts have been described in the literature of relating the effectiveness of DO with melting point [12]. Among the compounds studied the most effective DO—TBTU and DEBTU—at room temperature are liquids, while the other TU derivatives are crystalline products. However, a comparison of the protective action of DEHTU and EPHTU (Table 2) with their melting point and constant of reaction with ozone k_1 (Table 1) indicates that EPHTU at lower m.p. does not protect rubber at all from the effect of ozone in contrast to DEHTU—an effective DO. The k_1 value of these compounds is $0 \cdot 9 \times 10^6$ and $1 \cdot 6 \times 10^6$ mole/l.·sec, respectively.

The value of k_1 of THTU and DBHTU (Table 1) being equal, the latter is 3 times more effective as a DO which is, apparently, due to the different physical and chemical properties of these compounds (solubility in rubber, rate of diffusion in the surface, etc.).

Thus, the effect of the physical behaviour of compounds on their effects as DO cannot be excluded, but the role of these factors becomes noticeable with sufficient chemical activity of the compounds studied.

CONCLUSIONS

(1) 11 Tri-substituted thioureas (TU) were synthesized and rate constant of their reactions with ozone and their effectiveness as de-ozonizers (DO) in rubbers determined.

(2) It was shown that there is an exponential relation between the rate constant of reactions with ozone of several tri-substituted TU and their effectiveness as DO, which proves that the indirect reaction of TU with ozone is of considerable significance in the mechanism of action of these DO.

(3) The addition to the TU molecule of electron-donor substituents increases effectiveness.

(4) The physical properties of TU only influence the de-ozonizing effect of DO if the reaction rate of the compounds with ozone is fairly high.

Translated by E. Semere

REFERENCES

1. **A. Ye. GRINBERG, Ya. A. GURVICH, L. K. ZOLOTAREVSKAYA** and **A. M. LIPKIN**, Antiozonanty dlya svetlykh i tsvetnykh rezin (De-ozonizers for Light-coloured and Coloured Rubbers). TsNIITENeftekhim., 1969
2. Patent of the German Federal Republic, 1243864, 1967
3. **I. VATANABE**, Nippon Gomy Kyokaishi **41**: 7, 605, 1968
4. **A. M. LIPKIN, S. D. RAZUMOVSKII, A. Ye. GRINBERG, G. Ye. ZAIKOV** and **Ya. A. GURVICH**, Dokl. AN SSSR **192**: 127, 1970
5. **S. D. RAZUMOVSKII, L. M. REUTOVA, G. A. NIAZASHVILI, I. A. TUTORSKII** and **G. Ye. ZAIKOV**, Dokl. AN SSSR **194**: 1127, 1970; **S. D. RAZUMOVSKII**, Izv. AN SSSR, ser. khim., 335, 1970
6. **I. GUBEN**, Metody organicheskoi khimii (Methods of Organic Chemistry). 4, Izd. inostr. lit., 1949
7. Japanese patent 22194, 1965
8. **S. DUPIN** and **M. PESSON**, Bull. Soc. chim. France **88**, 144, 1963
9. **D. J. BEAVER, D. R. ROMAN** and **P. I. STOFFELL**, J. Amer. Chem. Soc. **79**, 1236, 1957
10. **A. ALCAIDE, A. M. MINICO** and **A. REBERA**, An. Real. soc. esp. Fis. y quim. **B62**: 1391, 1966
11. **A. M. LIPKIN, A. Ye. GRINBERG, Ya. A. GURVICH, L. K. ZOLOTAREVSKAYA, S. D. RAZUMOVSKII** and **G. Ye. ZAIKOV**, Vysokomol. soyed. **A14**: 78, 1972
12. **G. T. HODKINSON** and **C. E. KENDALL**, Proceedings of the Fourth Rubber Technology Conference, London, 1963