

## ADSORPTION AND CATALYTIC DECOMPOSITION OF 4-NITROBENZENESULPHONYLMETHYLCARBAMATE BY SMECTITE

PAOLO FUSI,<sup>1</sup> GIUSEPPE GABRIELE RISTORI,<sup>2</sup> AND MARCO FRANCI<sup>2</sup>

**Abstract**—Adsorption and catalytic decomposition of 4-nitrobenzenesulphonylmethylcarbamate (herbicide Nisulam) on Upton, Wyoming, bentonite saturated with different cations was studied using thin-layer chromatography and infrared spectroscopy. Nisulam is adsorbed at room temperature by coordination through the NO<sub>2</sub> group to the exchange cation regardless of the cation's nature. On moderate heating (75°–90°C) this molecule decomposes to 4-nitrobenzenesulphonamide whereas a similar compound (herbicide Asulam) containing the NH<sub>2</sub> functional group instead of NO<sub>2</sub> is adsorbed by protonation at room temperature and decomposes into different products. For cations having a high polarizing power, a coordination bond between the Asulam molecule's C=O group and the exchange cation is established, and the molecule decomposes to sulphanilic and carbamic acid. In contrast, for cations having a low polarizing power there is no coordination, and the molecule decomposes mainly into sulphanilamide. Nisulam's coordination to the exchange cation through the NO<sub>2</sub> group instead of C=O is ascribed to inductive and conjugation effects, typical of the nitro group.

**Key Words**—Adsorption, Asulam, Bentonite, Decomposition, Herbicide, Nisulam.

### INTRODUCTION

Catalytic decomposition of the herbicide Asulam (4-aminobenzenesulphonylmethylcarbamate—H<sub>2</sub>N-⊙-SO<sub>2</sub>-NH-CO-OCH<sub>3</sub>) adsorbed on Upton, Wyoming, bentonite saturated with different cations was described in previous papers (Fusi *et al.*, 1980; Ristori *et al.*, 1981; Fusi *et al.*, 1981). Asulam, adsorbed at room temperature by protonation of the -NH<sub>2</sub> group and physical forces, decomposes to sulphanilic, carbamic acid, sulphanilamide, or 4-aminobenzenesulphonylcarbamate on moderate heating. The nature of the principal reaction product was found to be related to the polarizing power of the clay's exchange cation. Where it is strong, the Asulam molecule coordinates to the cation through the C=O group and decomposes to sulphanilic and carbamic acid. In contrast, sulphanilamide and the 4-aminobenzenesulphonylcarbamate anion form in the absence of coordination. Because they affect adsorption and catalytic reactions on clay surfaces, the electron donor properties of the adsorbed molecule's single functional groups may be of some importance. Following the conclusions of several workers (Tahoun and Mortland, 1966; Mortland and Raman, 1967; Heller and Yariv, 1969; White, 1975; Cloos *et al.*, 1979) the substitution of one functional group by another should influence the type of bond formed between the organic molecule and the clay as well as the nature of the reaction product, regardless of the sol-

vation energy of the exchange cation. The aim of this paper is to examine the influence of substitution of NH<sub>2</sub> by NO<sub>2</sub> at the 4-position in the Asulam benzene ring on its adsorption and catalytic decomposition by montmorillonite. This NO<sub>2</sub>-substituted molecule, having properties similar to Asulam, is commonly called Nisulam.

### EXPERIMENTAL

#### Materials

Homoionic montmorillonites were prepared from a <2-μm fraction of Upton, Wyoming, bentonite. This was done by washing the clay with 1 M solutions of Al<sup>3+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Mg<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, K<sup>+</sup> and Li<sup>+</sup> and by removing excess salt until the Cl<sup>-</sup> test was negative. The Nisulam (4-nitrobenzenesulphonylmethylcarbamate, O<sub>2</sub>N-⊙-SO<sub>2</sub>-NH-CO-OCH<sub>3</sub>) was supplied by May and Baker, Ltd. The 4-nitrobenzenesulphonamide was prepared from a 4-O<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-SO<sub>2</sub>-Cl with concentrated ammonia solution, using the procedure described by Vogel (1961).

#### Infrared analysis

Thin, self-supporting homoionic clay films were prepared by air drying several milliliters of clay suspension placed on a polyethylene sheet. The films were peeled away carefully and immersed in a CCl<sub>4</sub>-saturated Nisulam solution for 24 hr. They were then removed from the solution, rinsed twice with CCl<sub>4</sub>, and air dried. Differential infrared (IR) spectra were recorded with the pure clay film on the reference beam to enhance the

<sup>1</sup> Istituto di Chimica Agraria e Forestale, Università di Firenze, Piazzale delle Cascine 28, Florence, Italy.

<sup>2</sup> Centro di Studio per i Colloidi del Suolo, C.N.R., Firenze, Piazzale delle Cascine 28, Florence, Italy.

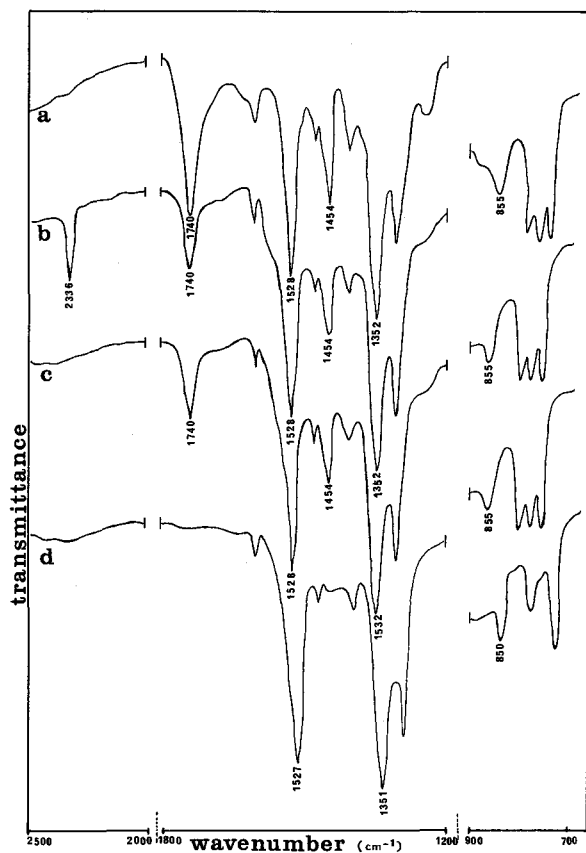


Figure 1. Differential infrared spectra of Nisulam-Al-montmorillonite complex: (a) at room temperature; (b) after heating at 75°C for 20 hr and then cooled in air for 10 min; (c) complex "b" equilibrated at 100% RH for 5 hr; (d) complex "c" heated at 90°C for 20 hr, then cooled in air.

bands which in the absolute spectra were obscured by lattice and/or water-clay vibrations at about 1640  $\text{cm}^{-1}$ . The spectra were recorded in the 2500–1200  $\text{cm}^{-1}$  and 900–700  $\text{cm}^{-1}$  regions. Different IR spectra of the Nisulam-clay systems were recorded at room temperature from: (1) the original sample, (2) the sample after heating at 75° and 90°C for 20 hr, and (3) after equilibrating the heated samples at 75°C and 100% RH for 5 hr.

#### Thin-layer chromatography

Fixed amounts of the original and heated Nisulam-clay complexes were extracted in ethanol. The solution was transferred to 0.2-mm silica gel 60 F<sub>254</sub> plastic sheets (Merck) and eluted with a 5:2 chloroform-methanol solution. Spots of the compound were revealed by a UV light. Similar experiments were performed with the pure compounds. The *r*F values determined were: 0.31 for Nisulam and 0.76 for 4-nitrobenzenesulphonamide. In addition, the single spots that resulted from eluting the solution and those from the clay-organic

complexes at different stages of the experiment were scraped off and extracted with ethanol. The residue was analyzed after the alcohol evaporated.

#### Chemical analysis

An evaluation of adsorbed Nisulam and its degradation products was carried out as follows: the Nisulam adsorbed at the outset of the experiment was determined by UV spectrophotometry at 268 nm after extraction in water of a fixed amount of clay. The decomposition product (4-nitrosulphonamide) was determined by scraping off the relevant spot which appeared on the chromatographic sheet at the end of the experiment. The scraped material was extracted with water, and nitrosulphonamide was determined by UV spectrophotometry at about 270 nm. CH<sub>3</sub>OH formation, as a degradation product of Nisulam clay complexes during heating, was tested with the nitrochromic acid method (Walsh and Merrit, 1960) following a procedure described by Fusi *et al.* (1980).

## RESULTS AND DISCUSSION

The main band assignments for the IR spectrum of Nisulam (KBr pellet) in the 2500–700  $\text{cm}^{-1}$  region are listed in Table 1. Unlike the findings obtained with Asulam (Fusi *et al.*, 1980; Ristori *et al.*, 1981; Fusi *et al.*, 1981), the spectra of Nisulam-montmorillonite complexes were practically identical regardless of the nature of the exchange cation. Therefore, only the IR spectra of Nisulam-Al-smectite complexes are reported in Figure 1.

About 35–45 mg/g clay of Nisulam was adsorbed at room temperature. The molecule adsorbed by coordination to the exchange cation through the NO<sub>2</sub> group as shown by the IR spectrum (Figure 1, spectrum "a"). The NO<sub>2</sub>-stretchings differ slightly, but significantly from those of Nisulam solid or of Nisulam in CHCl<sub>3</sub>. Asymmetric and symmetric stretchings are shifted respectively to lower frequencies by about 7–8  $\text{cm}^{-1}$  and to higher frequencies by about 4–5  $\text{cm}^{-1}$ . The NO<sub>2</sub> in plane symmetric deformation at about 850  $\text{cm}^{-1}$  is lower and broader compared to the corresponding band of the unadsorbed compound. Similar results were obtained with nitrobenzene and parathion adsorbed on montmorillonite (Saltzman and Yariv, 1976; Yariv *et al.*, 1966). According to Nakamoto (1978), the shift of both NO<sub>2</sub>-stretching bands to lower frequencies indicates that the nitro group's two oxygens are involved in the coordination bond. In contrast, the shifts towards opposite directions observed in our spectra, suggest that only one oxygen is bonded to the exchange cation through a water bridge. The following configuration is therefore suggested:

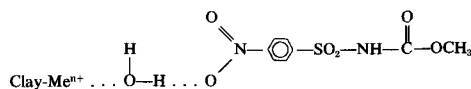
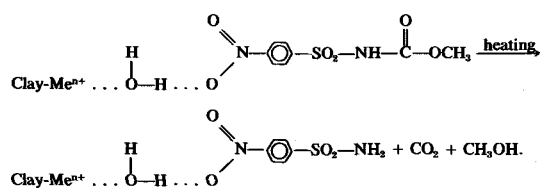


Table 1. Assignment of the principal bands in the infrared spectrum of Nisulam (KBr pellet) in the 2500–700  $\text{cm}^{-1}$  region.

Band position ( $\text{cm}^{-1}$ )	Band assignment	References
1741	C=O stretching	Bellamy, 1958; Rao, 1963
1610 } 1488 }	Benzene ring	Bellamy, 1958; Rao, 1963
1535 <sup>1</sup>		
1456	$\text{CH}_3$ bending	Tanaka and Tanaka, 1968; Exner <i>et al.</i> , 1972
1362	$\text{SO}_2$ asymmetric stretching	Carter and Devia, 1973
1348 <sup>1</sup>	$\text{NO}_2$ symmetric stretching	Tanaka and Tanaka, 1968; Exner <i>et al.</i> , 1972
1252	C–N stretching ( $\text{O}_2\text{N–C}$ )	—
1172	$\text{SO}_2$ symmetric stretching	Tanaka <i>et al.</i> , 1968
852	$\text{NO}_2$ symmetric in plane deformation (scissoring)	Exner <i>et al.</i> , 1972; Pinchas <i>et al.</i> , 1964

<sup>1</sup> These bands appear at 1534  $\text{cm}^{-1}$  and 1348  $\text{cm}^{-1}$  when Nisulam was dissolved in  $\text{CHCl}_3$ .

On heating the complex at 75°C the bands at 1740  $\text{cm}^{-1}$  and at 1454  $\text{cm}^{-1}$  respectively assigned to C=O-stretching and to  $\text{CH}_3$ -bending vibration decreased progressively. This was observed on all Nisulam-clay systems (Figure 1, spectrum "b"), while a new band at 2336  $\text{cm}^{-1}$ , assigned to  $\text{CO}_2$ -stretching vibration (Fripiat *et al.*, 1974), appeared in samples run no later than 10–20 min after heating. This compound probably derives from the decomposition reaction of Nisulam as reported below. After the subsequent equilibration at 100% RH, no changes were observed in the IR spectra (Figure 1, spectrum "c"). These findings, together with a positive nitrochromic test showing methylalcohol formation, indicate that smectite-adsorbed Nisulam decomposes as shown in the following reaction:



After further heating the sample at 90°C, Nisulam decomposed completely as indicated by chemical analysis and the disappearance of the C=O-, and  $\text{CH}_3$ -vibrational bands (Figure 1, spectrum "d"). Thin-layer chromatography of ethanol extracts of heated Nisulam-smectite complexes confirmed that only nitrobenzene-sulphonamide was present. Unlike the Asulam complexes, no traces of other compounds (e.g., 4-nitrobenzenesulphonic acid) were revealed using this method. Nisulam decomposition to 4-nitrobenzenesulphonamide is further supported by the similarity of the IR spectrum of this pure compound adsorbed on clay to that of the heated (90°C) Nisulam-clay system (Figure 2, spectrum "a").

## CONCLUSIONS

The substitution of a functional group in an organic molecule influences its adsorption on smectite and its catalytic decomposition. The Asulam molecule, having an  $\text{NH}_2$  functional group in position 4 on the ring, besides being protonated, is coordinated through the C=O group to exchange cations with comparatively high polarizing power. Coordination results in a weaker double bond character of the C=O group. The C–N bond is therefore strengthened, whereas the S–N bond is weakened. The latter thus becomes unstable, and Asulam decomposes into sulphanilic and carbamic acid. In contrast, in the absence of coordination, adsorbed Asulam decomposes to sulphanilamide if the unstable 4-aminobenzenesulphonylcarbamic acid, resulting from the preliminary hydrolysis of the  $-\text{CO}-\text{OCH}_3$  group, is not previously stabilized as a carbamate. This salt-formation process, occurring with exchange cations having low solvation energy ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ), can be ascribed to the relatively high pH ( $> \text{pK}_a$ ) determined in the interlayer spacing by these cations. The low environmental acidity probably produces the dissociation of the carboxylic group of the acid.

For Nisulam, where an  $\text{NO}_2$  group replaces  $\text{NH}_2$ , the inductive and conjugation effect (Gould, 1962) causes the molecule to coordinate to exchange cations through this nitro group, thereby precluding the bonding of the organic molecule through the C=O group. As a result, the double bond character of this group is preserved, and weakening of the S–N bond is precluded, as confirmed by the fact that only 4-nitrobenzenesulphonamide was formed as a reaction product in all the Nisulam-clay systems.

The absence of a 4-nitrobenzenesulphonylcarbamate anion, corresponding to a 4-aminobenzenesulphonylcarbamate anion which results from the Asulam de-

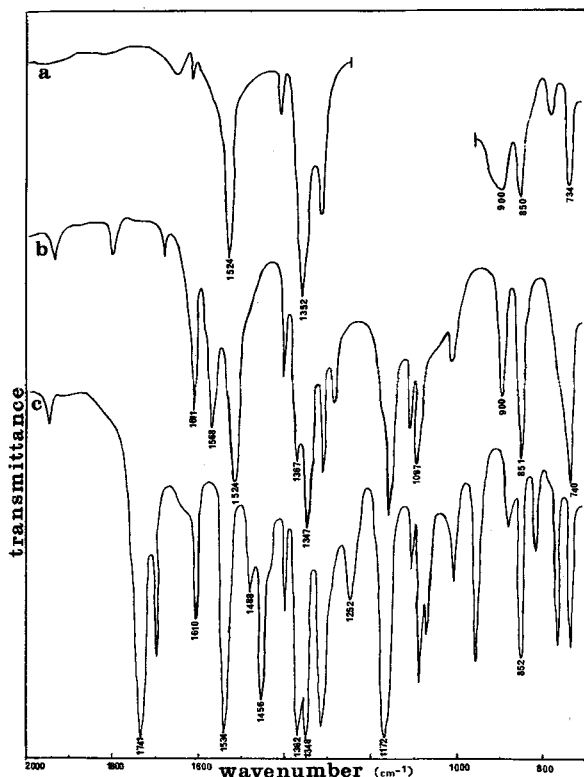


Figure 2. (a) Differential infrared spectrum of 4-nitrobenzenesulphonamide-Al-montmorillonite complex at room temperature; (b) absolute infrared spectrum of pure 4-nitrobenzenesulphonamide (KBr pellet); (c) absolute infrared spectrum of pure Nisulam (KBr pellet).

composition on alkaline montmorillonites, may depend on the cleavage of the C–N bond before hydrolysis of the  $-\text{CO}-\text{OCH}_3$  group. This reaction could be ascribed to the C–N weakening that results from electron withdrawing by the  $\text{NO}_2$  group which, on adsorbed Nisulam, is coordinated to the exchange cation at room temperature.

## REFERENCES

- Bellamy, L. J. (1958) *The Infrared Spectra of Complex Molecules*: Methuen, London, 64–160.
- Carter, J. C. and Devia, E. (1973) Vibrational analysis of methylcarbamate and *N,N*-dichloromethylcarbamate: *Spectrochim. Acta* **29A**, 623–632.
- Cloos, P., Moreale, A., Broer, C., and Badot, C. (1979) Adsorption and oxidation of aniline and *p*-chloroaniline by montmorillonite: *Clay Miner.* **14**, 307–321.
- Exner, O., Kovac, S., and Solcaniova, E. (1972) Substituent effects in infrared spectroscopy. II. Characteristic frequencies of the nitrogroup in meta and para-substituted nitrobenzenes: *Coll. Czech. Chem. Comm.* **37**, 2156–2168.
- Fripiat, J. J., Cruz, M. I., Bohor, B. F., and Thomas, J., Jr. (1974) Interlamellar adsorption of carbon dioxide by smectites: *Clays & Clay Minerals* **22**, 23–30.
- Fusi, P., Ristori, G. G., and Franci, M. (1981) Oxidative processes related to degradation of Asulam adsorbed on smectites: *Ann. Chim.* **71**, 443–451.
- Fusi, P., Ristori, G. G., and Malquori, A. (1980) Montmorillonite-Asulam interactions. I. Catalytic decomposition of Asulam adsorbed on H- and Al-clay: *Clay Miner.* **15**, 147–155.
- Gould, S. E. (1962) *Mechanism and Structure in Organic Chemistry*: Holt, Rinehart & Winston, New York, 200–218.
- Heller, L. and Yariv, S. (1969) Sorption of some anilines by Mn-, Co-, Ni-, Cu-, Zn-, and Cd-montmorillonite: *Proc. Int. Clay Conf., Tokyo, 1969, vol. 1*, L. Heller, ed., Israel Univ. Press, Jerusalem, 741–755.
- Mortland, M. M. and Raman, K. V. (1967) Catalytic hydrolysis of some organic phosphate pesticides by copper(II): *J. Agr. Food Chem.* **15**, 163–167.
- Nakamoto, K. (1978) *Infrared and Raman Spectra of Inorganic and Coordination Compounds*: 3rd ed., Wiley, New York, p. 225.
- Pinchas, S., Samuel, D., and Silver, B. L. (1964) The infrared adsorption spectrum of  $^{18}\text{O}$ -labeled nitrobenzene: *Spectrochim. Acta* **20**, 179–185.
- Rao, C. N. R. (1963) *Chemical Application of Infrared Spectroscopy*: Academic Press, New York, 156–195.
- Ristori, G. G., Fusi, P., and Franci, M. (1981) Montmorillonite-Asulam interactions. II. Catalytic decomposition of Asulam adsorbed on Mg-, Ba-, Ca-, Li-, Na-, K- and Cs-clay: *Clay Miner.* **16**, 125–137.
- Saltzman, S. and Yariv, S. (1976) Infrared and X-ray study of Parathion-montmorillonite sorption complexes: *Soil Sci. Soc. Amer. Proc.* **40**, 34–38.
- Tahoun, S. A. and Mortland, M. M. (1966) Complexes of montmorillonite with primary, secondary and tertiary amides: II. Coordination of amides on the surface of montmorillonite: *Soil Sci.* **102**, 314–321.
- Tanaka, Y. and Tanaka, Y. (1968) Infrared absorption spectra of organic sulfur compounds. IV. Studies on characteristic absorption bands of *o*-, *m*- and *p*-substituted benzenesulphonamide derivatives: *Yakugaku Zasshi* **88**, 695–698.
- Vogel, A. I. (1961) *A Text-Book of Practical Organic Chemistry Including Qualitative Organic Analysis*: Longmans, London, 543–544.
- Walsh, J. T. and Merrit, C. (1960) Qualitative functional group analysis of gas chromatographic effluents: *Anal. Chem.* **32**, 1378–1381.
- White, J. L. (1975) Protonation and hydrolysis of *s*-triazines by Ca-montmorillonite as influenced by substitution at the 2-, 4- and 6-positions: *Proc. Int. Clay Conf., Mexico City, 1975*, S. W. Bailey, ed., Applied Publishing, Wilmette, Illinois, 391–398.
- Yariv, S., Russell, J. D., and Farmer, V. C. (1966) Infrared study of the adsorption of benzoic acid and nitrobenzene in montmorillonite: *Israel J. Chem.* **4**, 201–213.

(Received 19 June 1981; accepted 17 October 1981)

**Резюме**—Адсорбция и каталитическая декомпозиция 4-нитробензеносульфони́лметилкарбоната (Гербицид Нисулам) бентонитом из Уптон, Лаеминг, насыщенным различными катионами, исследовалась путем хроматографии тонких слоев и инфракрасной спектроскопии. Нисулам адсорбируется в комнатной температуре путем координирования группы  $\text{NO}_2$  с обменным катионом независимо от типа этого катиона. При небольшом нагреве ( $75\text{--}90^\circ\text{C}$ ) молекула Нисулама раскладывается на 4-нитробензеносульфони́ламид, тогда как похожее соединение (гербицид Асулам), содержащее функциональную группу  $\text{NH}_2$  вместо  $\text{NO}_2$  адсорбируется путем протонирования в комнатной температуре и раскладывается на различные продукты. Для катионов с большой силой поляризации устанавливается координационная связь между группой  $\text{C}=\text{O}$  молекулы Асулана и обменным катионом, и молекула раскладывается на сульфаниловую и карбаминую кислоту. В противоположность, для катионов с низкой силой поляризации координация не выступает и молекула разлагается в основном на сульфаниламид. Координация Нисулама с обменным катионом посредством группы  $\text{NO}_2$  вместо двойной связи  $\text{C}=\text{O}$  приписана индуктивным и соединяющим эффектам, характерным для нитрогруппы. [E.C.]

**Resümee**—Es wurde die Adsorption und die katalytische Zersetzung von 4-Nitrobenzensulfonylmethylcarbammat (Herbizid Nisulam) durch ben Bentonit von Upton, Wyoming, der mit verschiedenen Kationen gesättigt war, mittels Dünnschichtchromatographie und Infrarotspektroskopie untersucht. Nisulam wird bei Raumtemperatur—unabhängig von der Art des Kations—durch die Koordination der  $\text{NO}_2$ -Gruppe mit dem austauschbaren Kation adsorbiert. Bei mäßigem Erhitzen ( $75\text{--}90^\circ\text{C}$ ) zerfällt dieses Molekül in 4-Nitrobenzensulfonamid während eine ähnliche Verbindung (Herbizid Asulam), die eine  $\text{NH}_2$ -funktionelle Gruppe anstelle der  $\text{NO}_2$ -Gruppe enthält, bei Raumtemperatur durch Protonierung adsorbiert wird und in verschiedene Produkte zerfällt. Bei Kationen, die ein großes Polarisierungsvermögen haben, bildet sich eine koordinative Bindung zwischen der  $\text{C}=\text{O}$ -Gruppe des Asulam-Moleküls und dem austauschbaren Kation, und das Molekül zerfällt in eine Sulfanilsäure und eine Carbaminsäure. Bei Kationen, die dagegen ein niedriges Polarisierungsvermögen haben, tritt keine Koordination auf und das Molekül zerfällt hauptsächlich in Sulfanilamid. Die Koordination von Nisulam an das austauschbare Kation durch die  $\text{NO}_2$ -Gruppe anstelle der  $\text{C}=\text{O}$ -Gruppe wird Induktions- und Konjugations-Effekten zugeschrieben, die für die  $\text{NO}_2$ -Gruppe typisch sind. [U.W.]

**Résumé**—On a étudié par chromatographie de fines couches et par spectroscopie infrarouge l'adsorption et la décomposition catalytique de nitrobenzènesulfonylméthylcarbamate-4 (l'herbicide Nisulam) sur une bentonite d'Upton, Wyoming, saturée de cations différents. Le Nisulam est adsorbé à température ambiante par coordination par le groupe  $\text{NO}_2$  au cation d'échange sans égards pour la nature du cation. Echauffée modérément ( $75\text{--}90^\circ\text{C}$ ), cette molécule se décompose en nitrobenzènesulphonamide-4, alors qu'un composé similaire (l'herbicide Asulam) contenant le groupe fonctionnel  $\text{NH}_2$  au lieu de  $\text{NO}_2$  est adsorbé par protonation à température ambiante et se décompose en produits différents. Pour des cations ayant une puissance polarisante élevée, un lien de coordination entre le groupe  $\text{C}=\text{O}$  de la molécule Asulam et le cation d'échange est établi, et la molécule se décompose en acides sulphanilique et carbamique. Par contraste, pour les cations ayant une puissance polarisante basse, il n'y a pas de coordination, et la molécule se décompose principalement en sulphanilamide. La coordination du Nisulam au cation d'échange par le groupe  $\text{NO}_2$  au lieu de  $\text{C}=\text{O}$  est assignée à des effets d'induction et de conjugaison typiques du groupe nitro. [D.J.]